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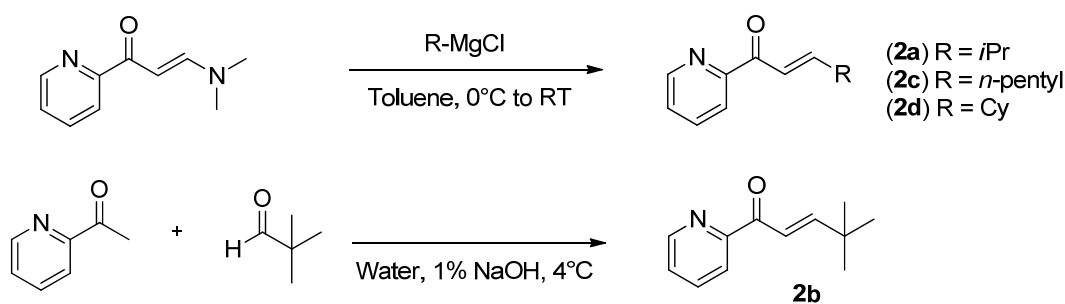
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An Enantioselective Artificial Metallo-Hydratase

Supporting info

Jeffrey Bos, Ana García-Herraz and Gerard Roelfes*

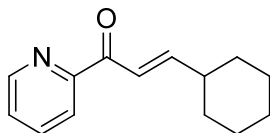
General remarks. Chemicals were purchased from Sigma Aldrich or Acros and used without further purification. Compound **2e** were prepared following published procedures.^[1] ¹H-NMR and ¹³C-NMR spectra were recorded on a Varian 400 (400 and 100 MHz), or Varian 300 (300 and 75 MHz) in CDCl₃ or DMSO-d₆. Chemical shifts (δ) are denoted in ppm using residual solvent peaks as internal standard (CDCl₃ δ_C = 77.16, δ_H = 7.26; DMSO δ_C = 39.52, δ_H = 2.50). Mass spectra (HRMS) were recorded on an Orbitrap XL (Thermo Fisher Scientific; ESI pos. mode). Enantiomeric excess determinations were performed by HPLC analysis using UV-detections (Shimadzu SCL-10Avp). Flash chromatography was performed using silica gel 60 Å (Merck, 200-400 mesh).



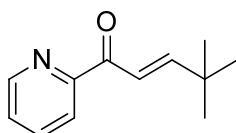
(E)-4-methyl-1-(pyridin-2-yl)pent-2-en-1-one (2a). Procedure adapted from literature^[2]. To a 50 mL flask filled with 30 mL of dry toluene was added 1.83 g (10.4 mmol) 3-(Dimethylamino)-1-(2-pyridyl)-2-propen-1-one and the solution was cooled to 0°C under nitrogen. 9.3 mL (12.5 mmol, 1.25 eq) of a 2 M solution of isopropylmagnesium chloride in THF was added slowly. The solution was stirred at room temperature overnight. Solvent was removed by evaporation and the solid was dissolved in 150 mL dichloromethane and hydrolyzed with 250 mL water under vigorous stirring. 2 gr of sodium bicarbonate was added and the organic phase was separated. The aqueous phase was extracted three times with dichloromethane (50 mL). The combined organic phases were washed successively with a saturated bicarbonate solution, water and a saturated sodium chloride solution and then dried over sodium sulfate. Concentration in vacuo, and purification by flash column chromatography (SiO₂, EtOAc:pentane, gradient) yielding **2a** (0.7 g; 40%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.69 – 8.61 (m, 1H), 8.11 – 8.03 (m, 1H), 7.83 – 7.75 (m, 1H), 7.52 (dd, *J* = 15.8, 1.4, 1H), 7.44 – 7.36 (m, 1H), 7.16 (dd, *J* = 15.8, 6.8, 1H), 2.66 – 2.46 (m, 1H), 1.10 (d, *J* = 6.8, 6H). ¹³C NMR (101 MHz, CDCl₃) δ = 189.88, 156.38, 154.33, 148.84, 136.96, 126.76, 122.89, 121.67, 31.71, 21.45, 18.72. Exact mass (HRMS) calcd for C₁₁H₁₄NO (MH⁺) 176.1070, found 176.1070.

(E)-1-(pyridin-2-yl)oct-2-en-1-one (2c). Procedure as for **2a**. 9.3 mL (12.5 mmol, 1.25 eq) of a 2 M solution of pentylmagnesium chloride solution chloride in THF was added slowly. Concentration in vacuo, and purification by flash column

chromatography (SiO₂, EtOAc:pentane, gradient) yielded **2c** (1.2 g; 56%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.74 – 8.52 (m, 1H), 8.14 – 8.04 (m, 1H), 7.85 – 7.73 (m, 1H), 7.61 – 7.50 (m, 1H), 7.46 – 7.34 (m, 1H), 7.29 – 7.13 (m, 1H), 2.40 – 2.18 (m, 2H), 1.58 – 1.42 (m, 2H), 1.37 – 1.20 (m, 4H), 0.85 (dd, *J* = 7.1, 5.6, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 189.42, 154.18, 150.50, 148.72, 136.88, 126.65, 124.34, 122.82, 32.91, 31.43, 27.83, 22.42, 13.93. Exact mass (HRMS) calcd for C₁₃H₁₈NO (MH⁺) 204.1383, found 204.1384.

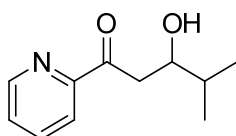


(E)-3-cyclohexyl-1-(pyridin-2-yl)prop-2-en-1-one (2d). Procedure as for **2a**. 9.3 mL (12.5 mmol, 1.25 eq) of a 2 M solution of pentylmagnesium chloride solution chloride in diethylether was added slowly. Concentration in vacuo, and purification by flash column chromatography (SiO₂, EtOAc:pentane, gradient) yielded **2d** (0.9 g; 40 %) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.73 – 8.63 (m, 1H), 8.14 – 8.03 (m, 1H), 7.86 – 7.75 (m, 1H), 7.59 – 7.49 (m, 1H), 7.47 – 7.37 (m, 1H), 7.22 – 7.08 (m, 1H), 2.37 – 2.16 (m, 1H), 1.87 – 1.70 (m, 4H), 1.70 – 1.60 (m, 1H), 1.36 – 1.11 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ = 189.81, 155.11, 154.27, 148.74, 136.85, 126.63, 122.79, 121.89, 41.15, 31.76, 25.95, 25.73. Exact mass (HRMS) calcd for C₁₄H₁₈NO (MH⁺) 216.1383, found 216.1383.

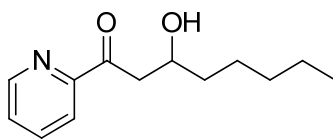


(E)-4,4-dimethyl-1-(pyridin-2-yl)pent-2-en-1-one (2b). Procedure adapted from literature^[3]. To a 100 mL flask filled with 75 mL of water was added 1.5 g (12 mmol) 2-acetylpyridine and 1.0 g (11.6 mmol) pivaldehyde at 0°C. To the suspension was added 7 mL of a 10% NaOH solution. The mixture was shaken vigorously and left undisturbed overnight at 4°C. The aqueous phase was extracted three times with dichloromethane (50 mL). The combined organic phases were washed successively with a saturated bicarbonate solution, water and a saturated sodium chloride solution and then dried over sodium sulfate. Concentration in vacuo, and purification by flash column chromatography (SiO₂, EtOAc:pentane, gradient) yielded **2b** (0.24 g; 10%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.74 – 8.66 (m, 1H), 8.11 (d, *J* = 7.9, 1H), 7.89 – 7.75 (m, 1H), 7.54 (d, *J* = 15.9, 1H), 7.49 – 7.40 (m, 1H), 7.24 (d, *J* = 15.8, 1H), 1.17 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ = 190.09, 159.94, 154.35, 148.78, 136.87, 126.65, 122.84, 119.38, 34.32, 28.75. Exact mass (HRMS) calcd for C₁₂H₁₆NO (MH⁺) 190.1226, found 190.1227.

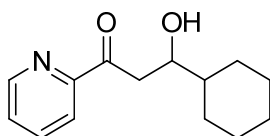
General procedure for the preparation of the water addition products as reference compounds. To 1 L of 20 mM MOPS buffer pH 6.5 was added, 200 mg of the substrate (pre dissolved in 5 mL CH₃CN) and 60 mg of Cu-Phenatrolin^[3]. The reaction was stirred for 12 hours at room temperature and the product was extracted with diethyl ether (3 x 50 mL), washed with saturated sodium chloride and dried over sodium sulfate. Concentration in vacuo of the organic layer was followed by purification by column chromatography.



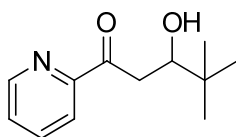
3-hydroxy-4-methyl-1-(pyridin-2-yl)pentan-1-one (3a). ¹H NMR (400 MHz, CDCl₃) δ 8.72 – 8.62 (m, 1H), 8.09 – 8.03 (m, 1H), 7.89 – 7.83 (m, 1H), 7.52 – 7.45 (m, 1H), 3.96 – 3.84 (m, 1H), 3.38 – 3.21 (m, 2H), 1.90 – 1.70 (m, 1H), 1.00 (dd, *J* = 6.8, 4.1, 7H). ¹³C NMR (101 MHz, CDCl₃) δ = 202.44, 153.41, 148.91, 137.38, 127.49, 122.24, 72.91, 42.90, 33.83, 18.60, 17.92. Exact mass (HRMS) calcd for C₁₁H₁₆NO₂ (MH⁺) 194.1176, found 194.1177. The *ee* was determined by HPLC analysis (Chiralpak-ASH, n-heptane:iPrOH 99.5:0.5, 0.5 ml/min). Retention times: 34.0 min and 37.5 min.



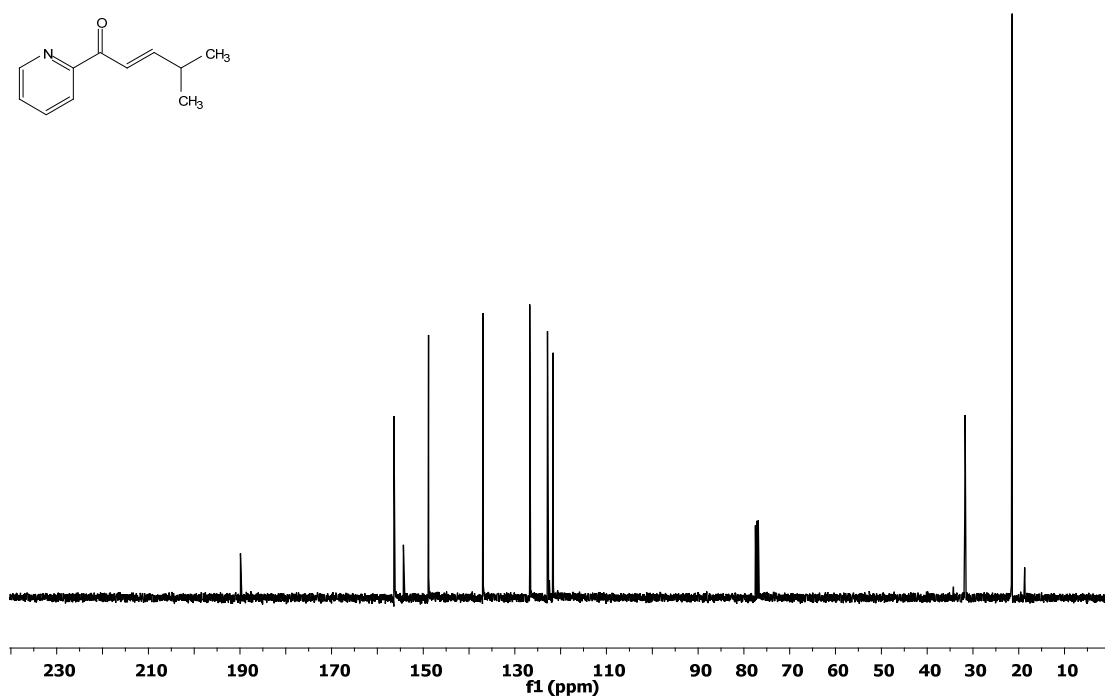
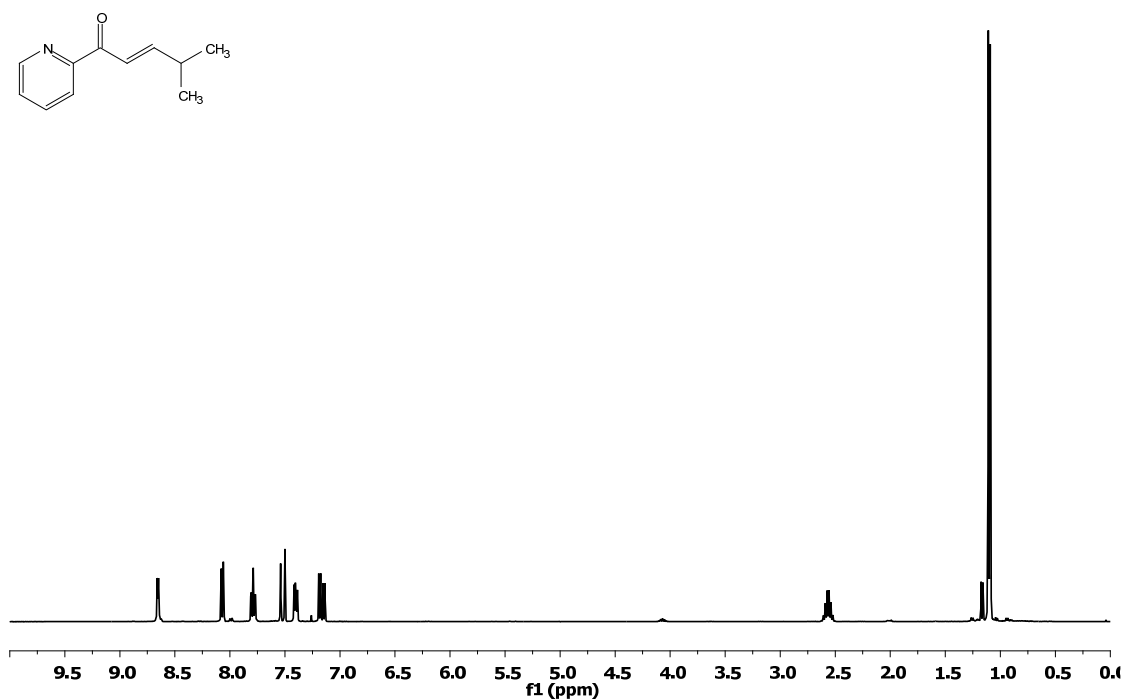
3-hydroxy-1-(pyridin-2-yl)octan-1-one (3c). ^1H NMR (400 MHz, CDCl_3) δ 8.73 – 8.62 (m, 1H), 8.11 – 7.99 (m, 1H), 7.91 – 7.80 (m, 1H), 7.54 – 7.44 (m, 1H), 4.24 – 4.08 (m, 1H), 3.84 (bs, 1H), 3.40 (dd, J = 16.8, 2.5, 1H), 3.24 (dd, J = 16.8, 9.0, 1H), 1.76 – 1.18 (m, 8H), 0.88 (t, J = 6.9, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ = 201.99, 153.20, 148.79, 137.19, 127.35, 122.04, 68.04, 45.50, 37.04, 31.79, 25.24, 22.61, 14.03. Exact mass (HRMS) calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_2$ (MH^+) 222.1489, found 222.1489. The *ee* was determined by HPLC analysis (Chiralpak-ODH, n-heptane:iPrOH 99:1, 0.5 ml/min). Retention times: 37.0 min and 49.6 min.

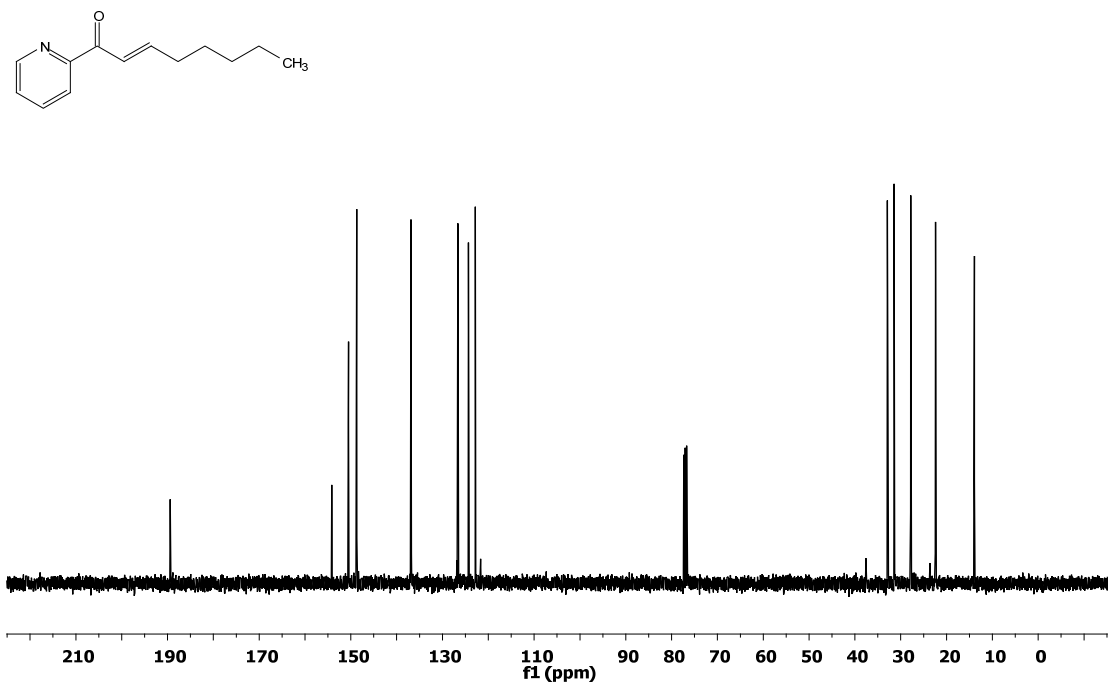
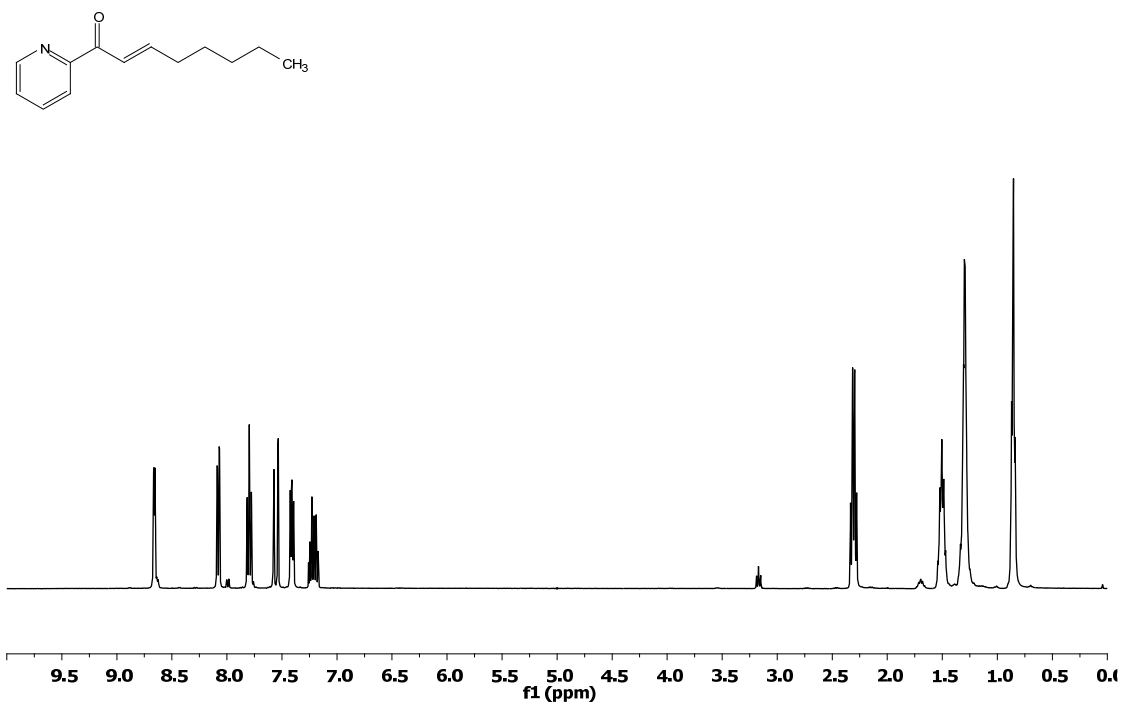


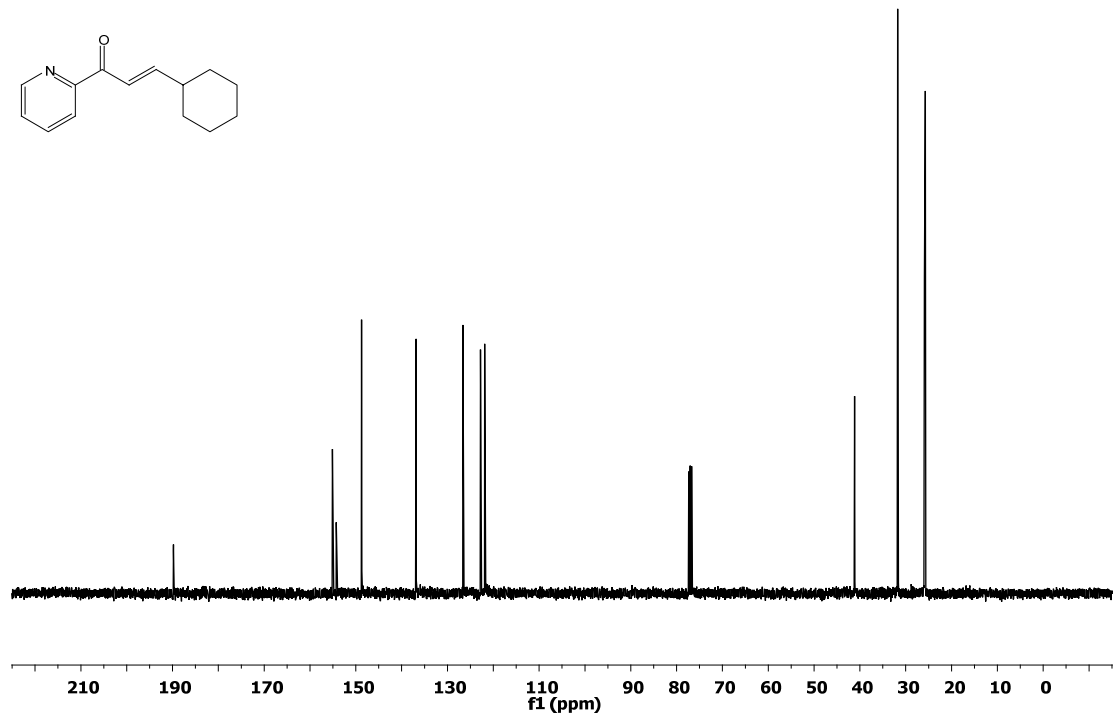
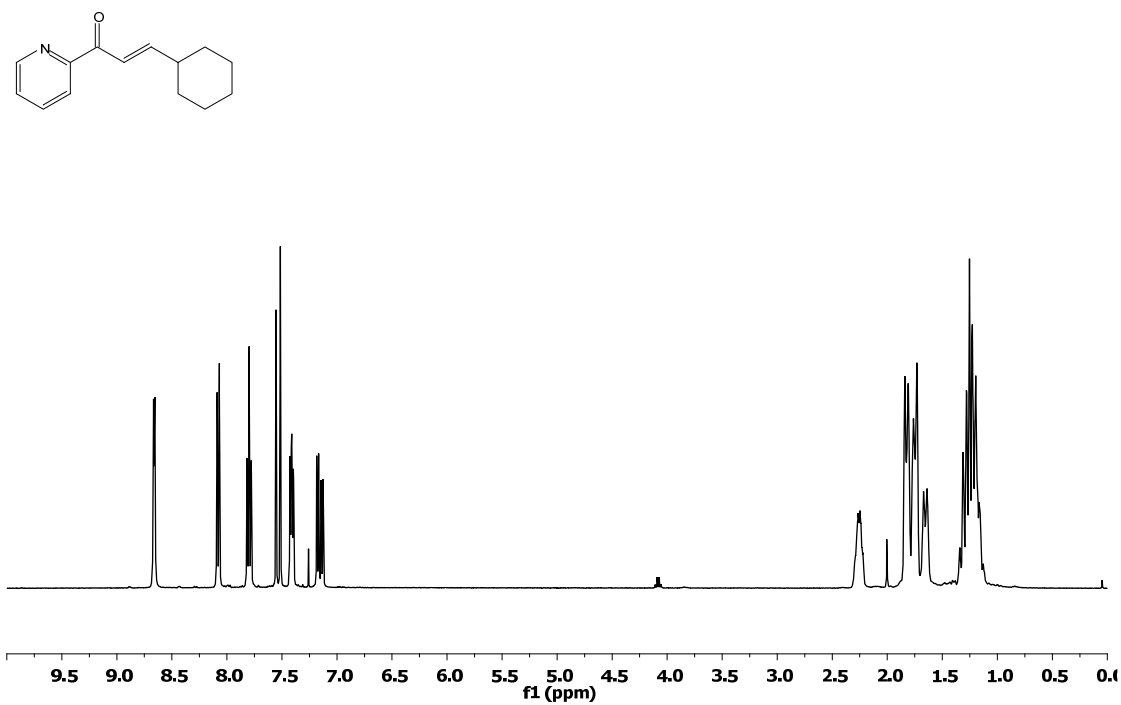
3-cyclohexyl-3-hydroxy-1-(pyridin-2-yl)propan-1-one (3d). ^1H NMR (400 MHz, CDCl_3) δ 8.77 – 8.60 (m, 1H), 8.05 (d, J = 7.9, 1H), 7.89 – 7.79 (m, 1H), 7.57 – 7.43 (m, 1H), 3.96 – 3.88 (m, 1H), 3.77 (bs, 1H), 3.45 – 3.21 (m, 2H), 1.92 (d, J = 12.1, 1H), 1.83 – 1.71 (m, 4H), 1.71 – 1.61 (m, 1H), 1.53 – 1.39 (m, 1H), 1.32 – 1.04 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ = 202.39, 153.28, 148.77, 137.17, 127.31, 122.03, 72.14, 43.63, 42.80, 28.91, 28.21, 26.50, 26.24, 26.15. Exact mass (HRMS) calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_2$ (MH^+), 234.1489 found 234.1490. The *ee* was determined by HPLC analysis (Chiralpak-ODH, n-heptane:iPrOH 99:1, 0.5 ml/min). Retention times: 40.6 min and 46.6 min.

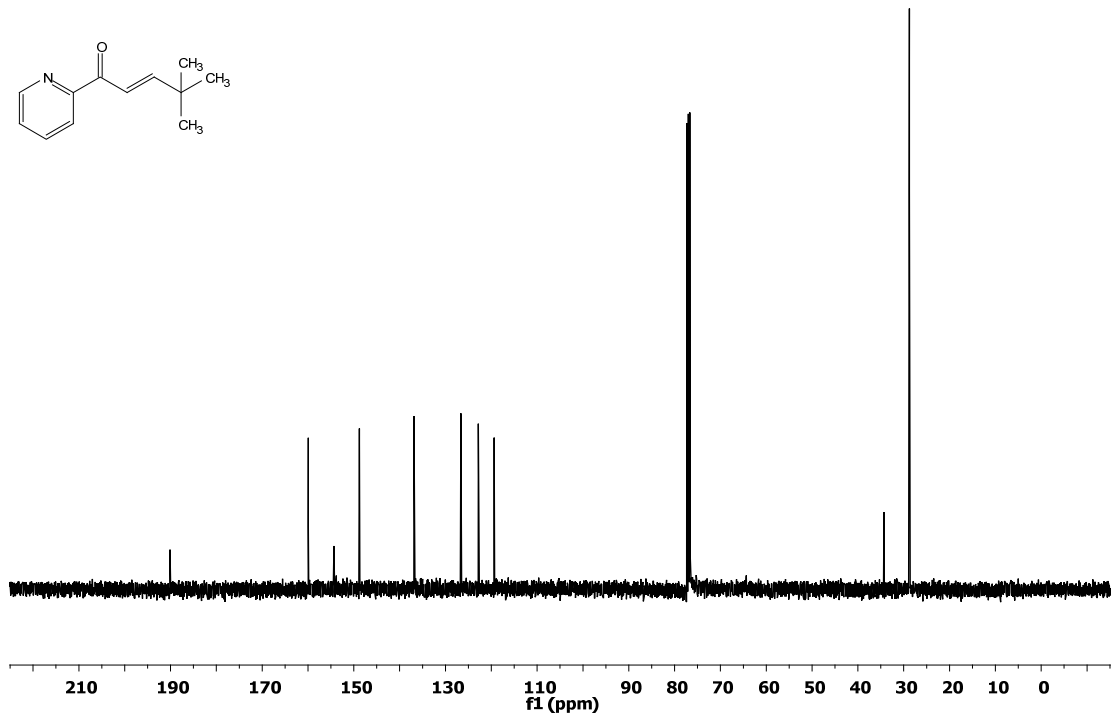
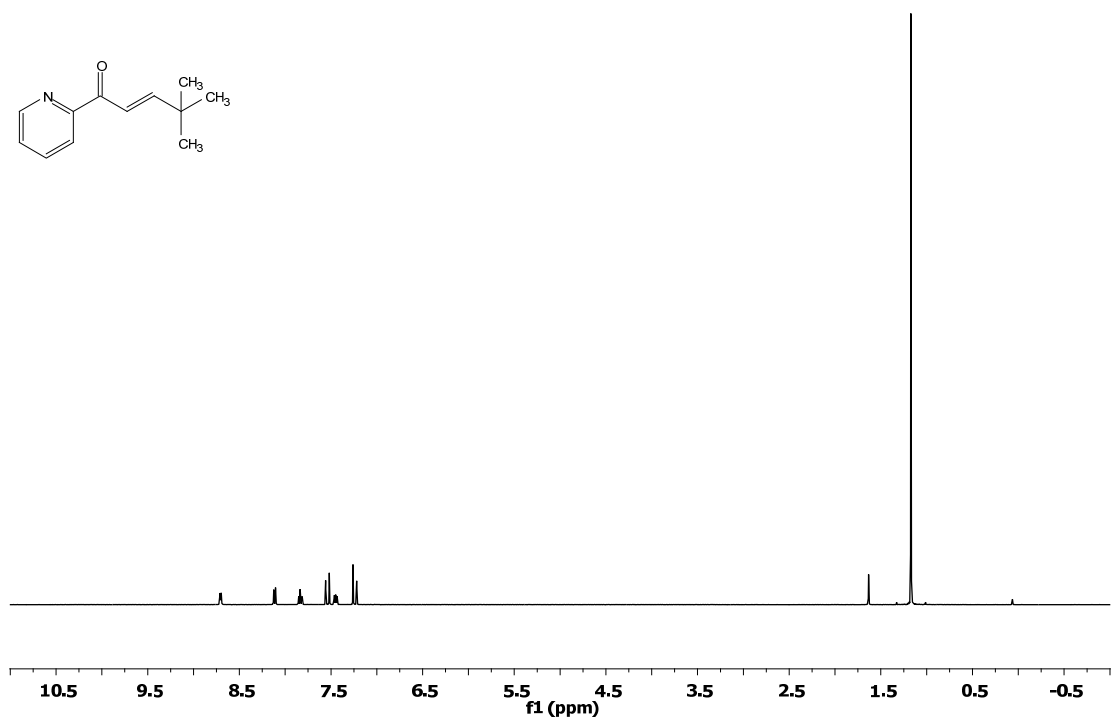


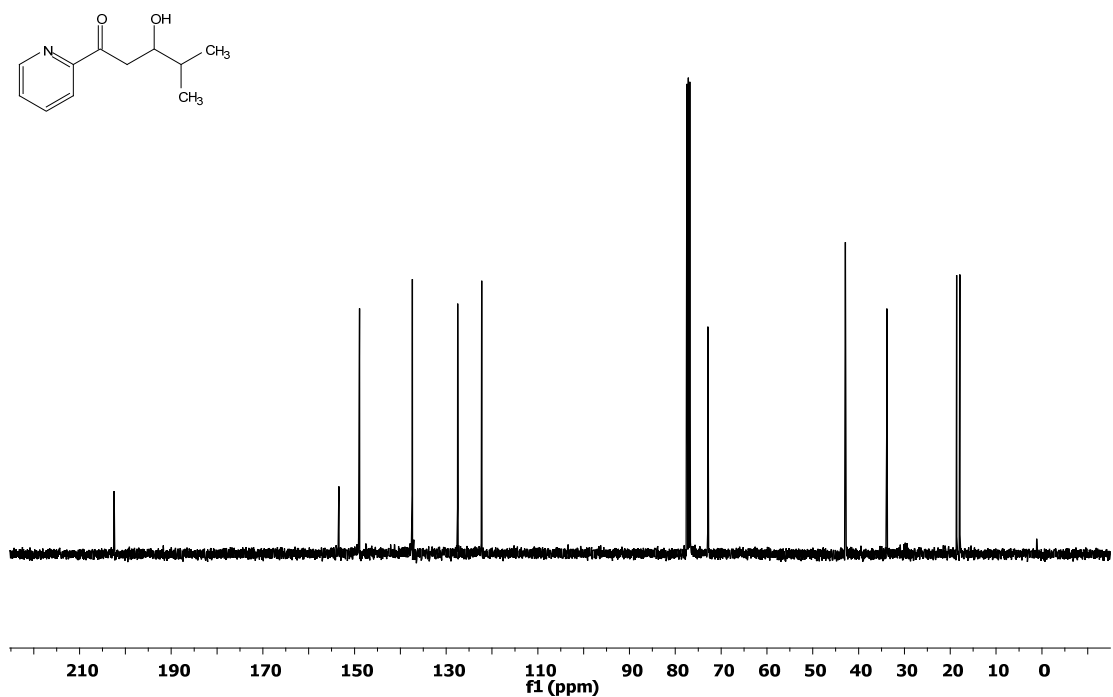
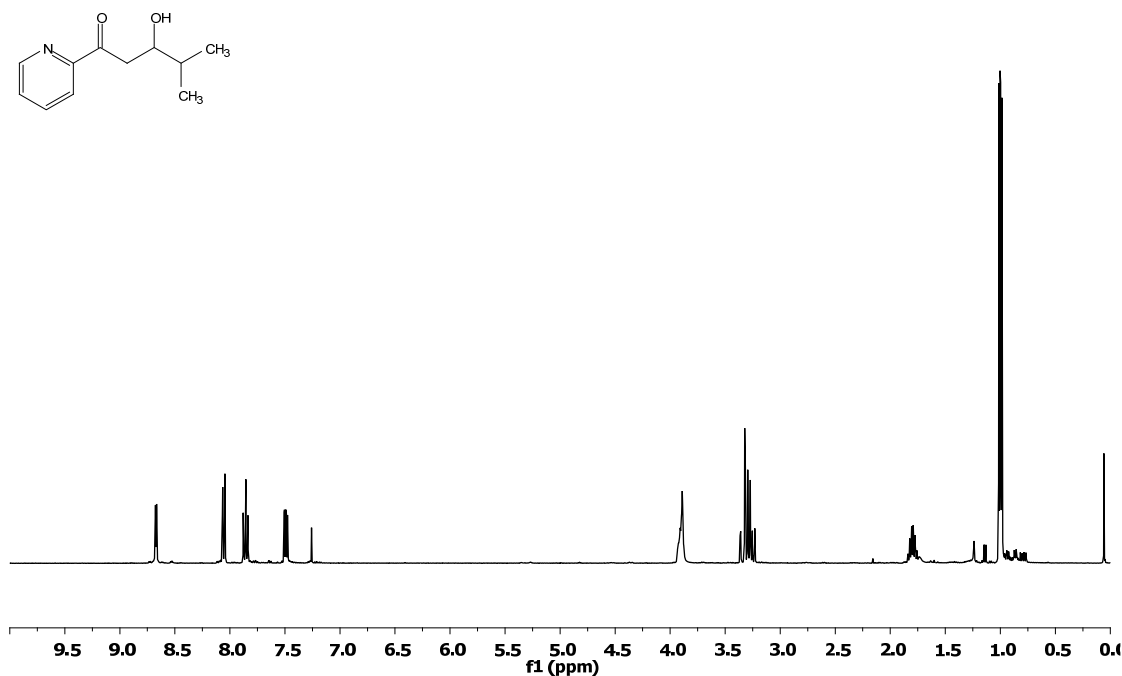
3-cyclohexyl-3-hydroxy-1-(pyridin-2-yl)propan-1-one (3b). ^1H NMR (300 MHz, CDCl_3) δ 8.68 (d, J = 4.4, 1H), 8.07 (d, J = 7.8, 1H), 7.86 (d, J = 1.5, 1H), 7.57 – 7.43 (m, 1H), 3.86 (s, 1H), 3.80 (d, J = 9.7, 1H), 3.30 (dd, J = 18.2, 5.8, 2H), 1.00 (s, 9H). ^{13}C NMR (50 MHz, CDCl_3) δ = 202.52, 153.37, 148.73, 137.20, 127.27, 122.09, 75.58, 40.92, 34.82, 25.70. Exact mass (HRMS) calcd for $\text{C}_{14}\text{H}_{18}\text{NO}_2$ (MH^+) 208.1332, found 208.1334. The *ee* was determined by HPLC analysis (Chiralpak-ADH, n-heptane:iPrOH 99:1, 0.5 ml/min). Retention times: 53.8 min and 61.4 min.

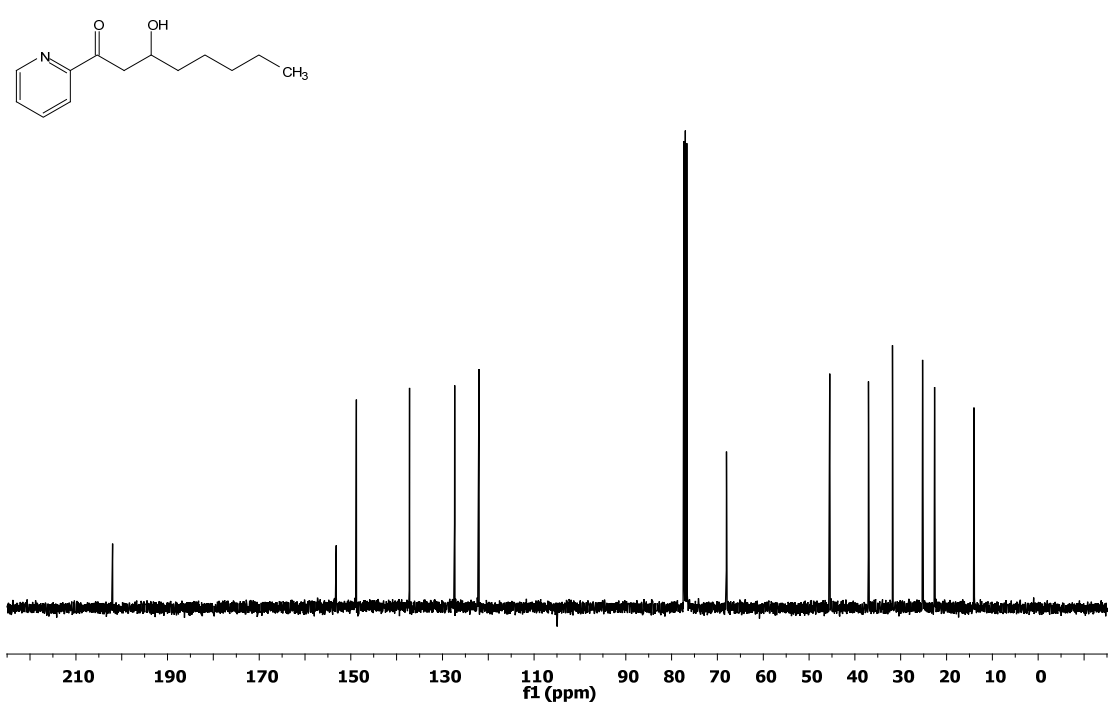
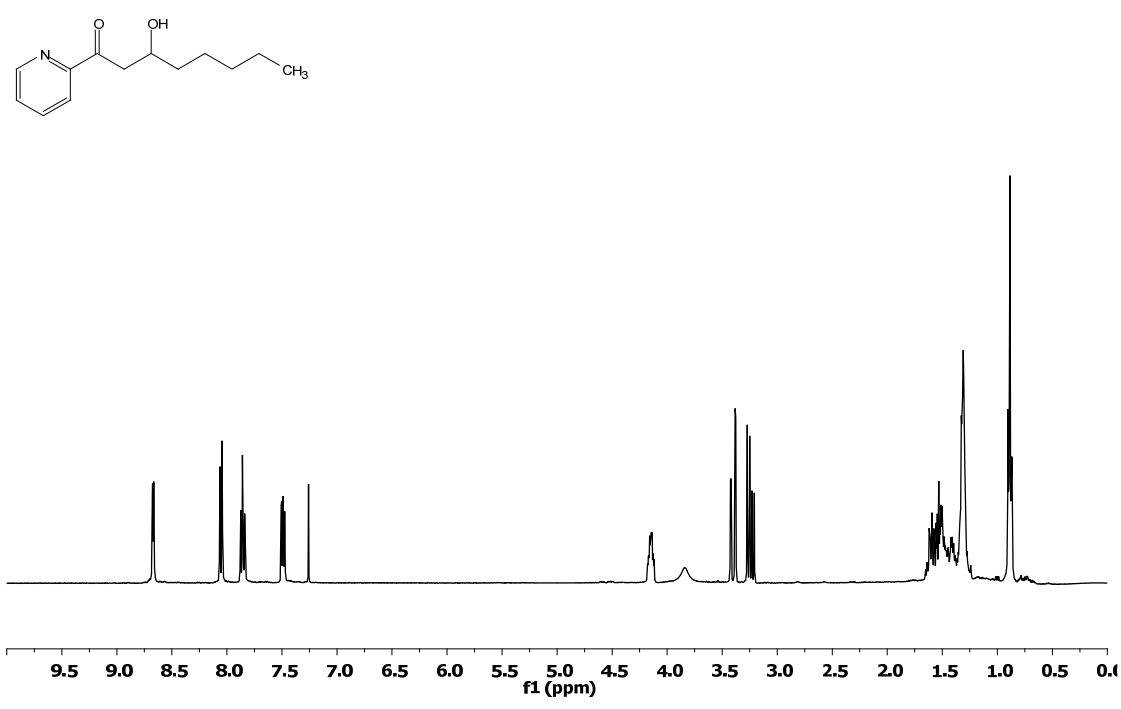


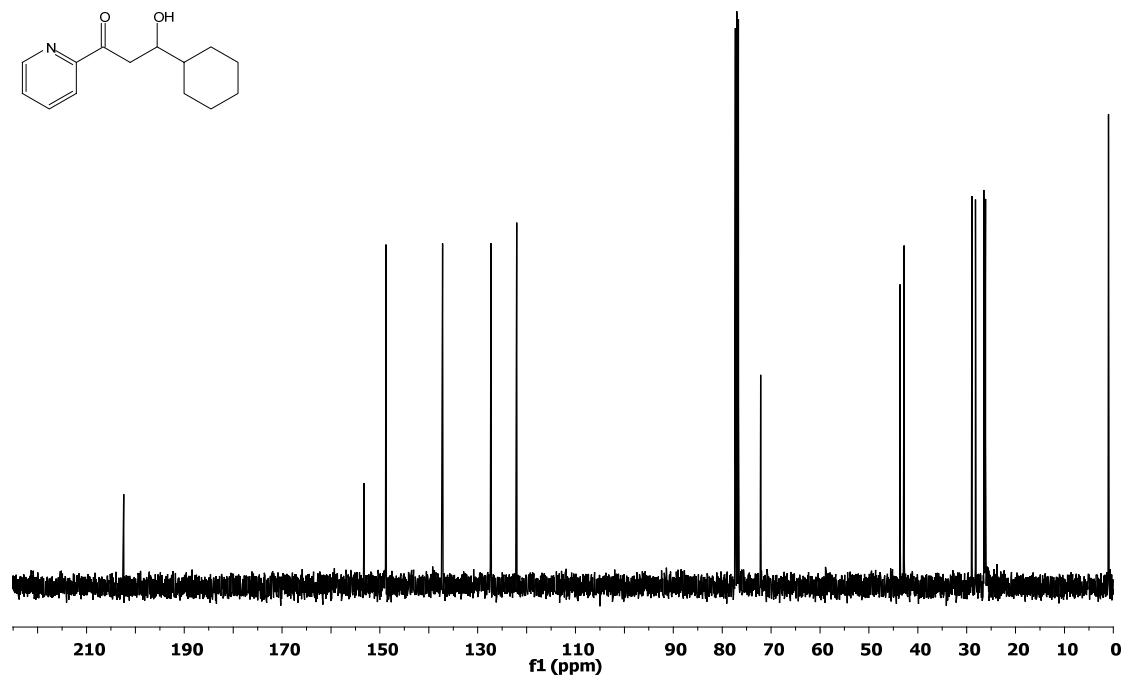
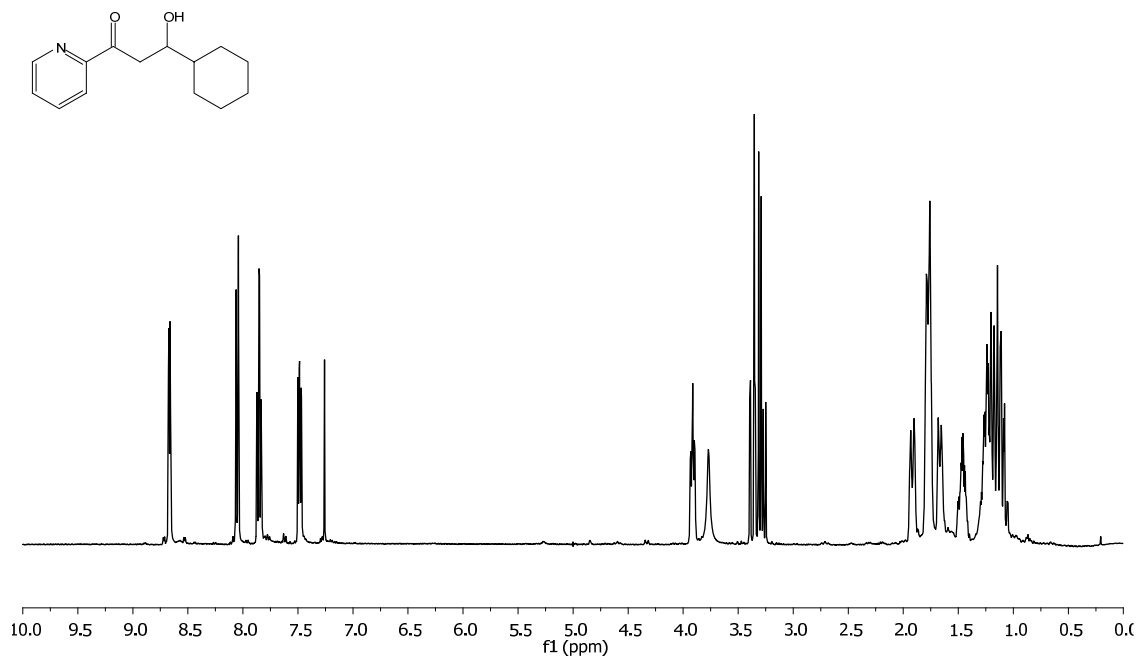


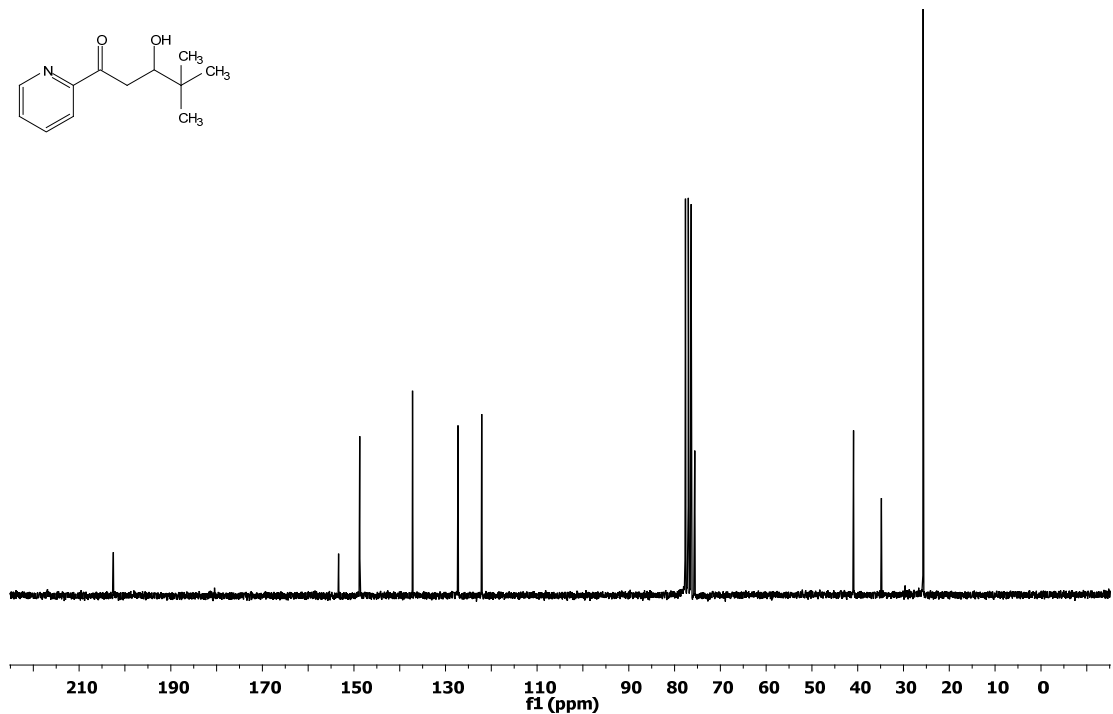
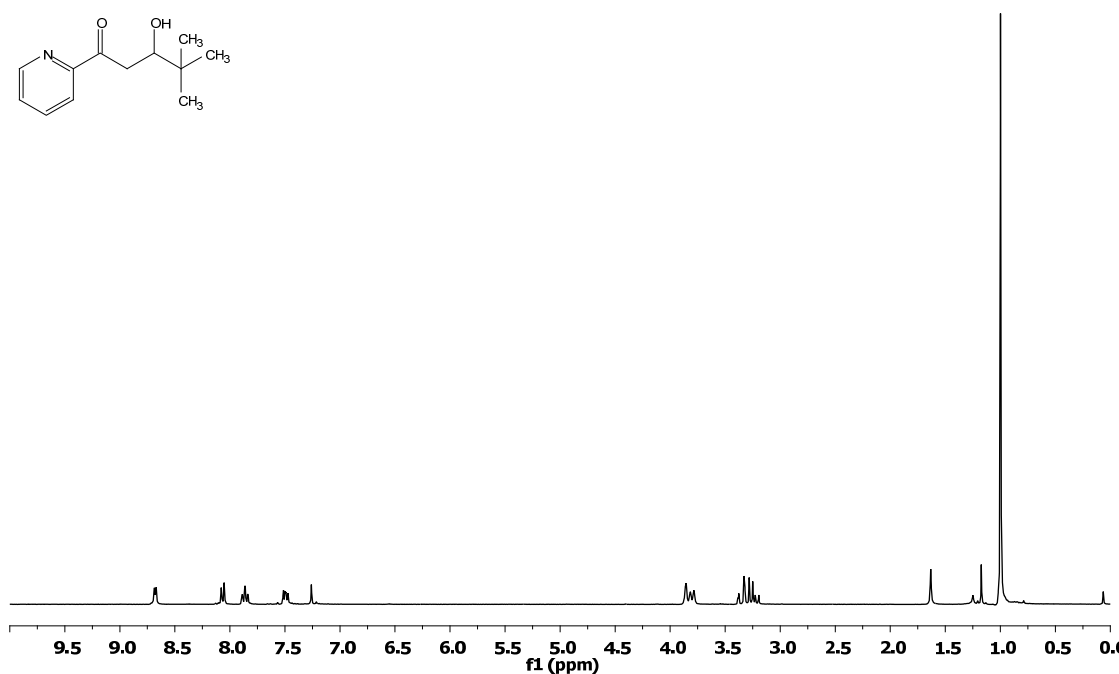












General remarks *E. coli* strains XL-1-Blue and BL21 (DE3)_C43 (Stratagene) were used for routine cloning and protein production, respectively. PCR reactions were carried out using an Eppendorf Mastercycler Personal apparatus. DNA sequencing was carried out by GATC-Biotech (Berlin, Germany). Primers were synthesized by Eurofins MWG Operon (Ebersberg, Germany). Restriction endonucleases were purchased from New England Biolabs. T4 DNA ligase, DNA Gel Extraction Kit and Plasmid Purifying Kit were purchased from Roche. *Pfu* Turbo polymerase was purchased from Stratagene. FPLC columns were purchased from GE Healthcare.

Construction of expression plasmid pET17b_LmrR. The LmrR gene (derived from *L. lactis* MG1363) including a C-terminal Strep-tag, was amplified by PCR using the following primers; primer 1: 5'-TACTACCATATGGGGGCAGAAATACCAAAGAAA-3' (including *NdeI* restriction site, underlined), primer 2: GTAGTACTCGAGAAGCTTTTATTTTCGAAGTGGGGT (including *XhoI* restriction site, underlined). PCR cycles were as following: initial denaturation at 94 °C for 5 min. Denaturation at 94 °C for 1 min, annealing at 45 °C for 45 sec., extension at 72 °C for 90 sec., for 30 cycles. Final extension at 72 °C for 5 min. The obtained PCR product was digested with *NdeI* and *XhoI*, and inserted between the same sites of the expression vector pET17b.

Site directed mutagenesis. Site directed mutagenesis was performed on the pET17b_LmrR plasmid. Primers used for preparing the mutants are shown in table 1. PCR cycles were as following: initial denaturation at 95 °C for 30 sec. Denaturation at 95 °C for 30 sec., annealing at 55 °C for 1 min., extension at 68 °C for 3.5 min., for 16 cycles. The obtained PCR product was digested with *DpnI* and used for transformation to *E.coli* XL-1-Blue without further purification.

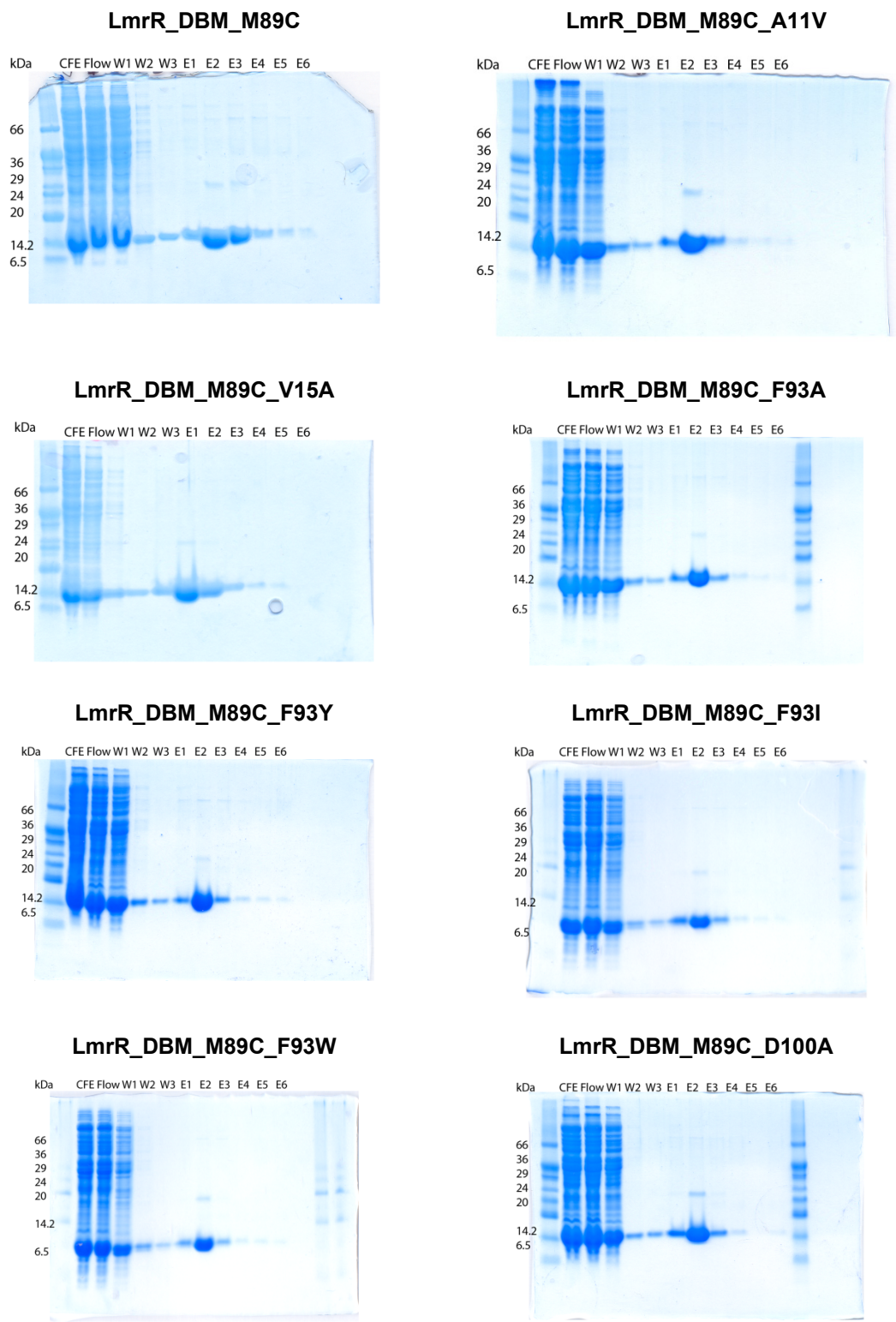
Table S1: PCR primers used for directed mutagenesis

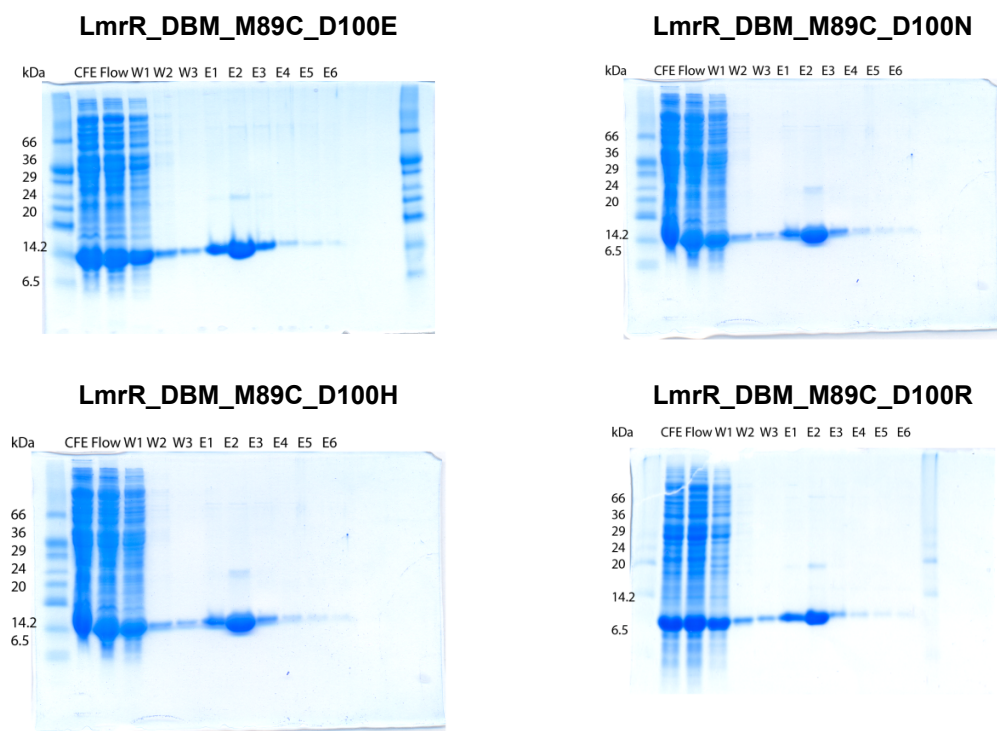
Primer	Sequence (5' -> 3')
LmrR_M89C_K55D_K59Q_fw	G CTC TAT ACG ATC TTT GAT AGA CTT GAA CAG GAT GGG ATT ATC AG
LmrR_M89C_K55D_K59Q_rv	CTG ATA ATC CCA TCC TGT TCA AGT CTA TCA AAG ATC GTA TAG AGC
LmrR_M89C_K55D_K59Q_A11V_fw	GAA ATG TTA CGA GTC CAA ACC AAT GTA ATT TTG
LmrR_M89C_K55D_K59Q_A11V_rv	CAA AAT TAC ATT GGT TTG GAC TCG TAA CAT TTC
LmrR_M89C_K55D_K59Q_V15A_fw	CGA GCC CAA ACC AAT GCA ATT TTG CTC AAT GTC C
LmrR_M89C_K55D_K59Q_V15A_rv	GGA CAT TGA GCA AAA TTG CAT TGG TTT GGG CTCG
LmrR_M89C_K55D_K59Q_F93A_fw	GCC GAC TTG CCG CGG AAT CTT GGT CAA G
LmrR_M89C_K55D_K59Q_F93A_rv	CTT GAC CAA GAT TCC GCG GCA AGT CGG C
LmrR_M89C_K55D_K59Q_F93Y_fw	GCC GAC TTG CCT ATG AAT CTT GGT CAA G
LmrR_M89C_K55D_K59Q_F93Y_rv	CTT GAC CAA GAT TCA TAG GCA AGT CGG C
LmrR_M89C_K55D_K59Q_F93I_fw	GCC GAC TTG CCA TTG AAT CTT GGT CAA G
LmrR_M89C_K55D_K59Q_F93I_rv	CTT GAC CAA GAT TCA ATG GCA AGT CGG C
LmrR_M89C_K55D_K59Q_F93W_fw	GCC GAC TTG CCT GGG AAT CTT GGT CAA G
LmrR_M89C_K55D_K59Q_F93W_rv	CTT GAC CAA GAT TCC CAG GCA AGT CGG C
LmrR_M89C_K55D_K59Q_D100A_fw	GAA TCT TGG TCA AGA GTC GCC AAA ATT ATT GAA AAT TTA G
LmrR_M89C_K55D_K59Q_D100A_rv	CTA AAT TTT CAA TAA TTT TGG CGA CTC TTG ACC AAG ATT C
LmrR_M89C_K55D_K59Q_D100E_fw	GGT CAA GAG TCG AAA AAA TTA TTG AAA ATT TAG AAG C
LmrR_M89C_K55D_K59Q_D100E_rv	GCT TCT AAA TTT TCA ATA ATT TTT TCG ACT CTT GAC C
LmrR_M89C_K55D_K59Q_D100N_fw	GAA TCT TGG TCA AGA GTC AAT AAA ATT ATT GAA AAT TTA G
LmrR_M89C_K55D_K59Q_D100N_rv	CTA AAT TTT CAA TAA TTT TAT TGA CTC TTG ACC AAG ATT C
LmrR_M89C_K55D_K59Q_D100H_fw	GAA TCT TGG TCA AGA GTC CAT AAA ATT ATT GAA AAT TTA G
LmrR_M89C_K55D_K59Q_D100H_rv	CTA AAT TTT CAA TAA TTT TAT GGA CTC TTG ACC AAG ATT C

Expression and purification. Protein expression plasmids of the LmrR constructs were transformed into *E. coli* BL21 (DE3)_C43 and a single colony was inoculated into a starter culture of 10 mL of fresh LB medium containing 100 µg/mL of ampicillin. 10 mL of starter culture was used to inoculate 1 L of fresh LB medium containing 100 µg/mL of ampicillin. When

the culture reached the mid-log phase (optical density at 600 nm around 0.6–0.8) isopropyl β -D-1-thiogalactopyranoside (IPTG) at final concentration of 1 mM was added to induce the expression of target protein. Expressions were done at 30 °C overnight. Cells were harvested by centrifugation (6000 rpm, JA10, 25 min, 4 °C, Beckman), and washed with 50 mM NaH_2PO_4 , pH 8.0, 150 mM NaCl, 2.5 mM DTT (DTT was added in the case of the cysteine mutants), and 10% glycerol. The resulting pellet was frozen at -20 °C overnight. The pellet was resuspended in the same buffer as was used for washing and sonicated (75% (200W) for 5 min (10 sec on, 10 sec off)). The lysed cells were incubated with DNaseI (0.1 mg/mL, containing final concentration 10 mM MgCl_2) for 1 hour at 30 °C. After centrifugation (15000 rpm, JA-17, 1h, 4 °C, Beckman), the supernatant was equilibrated with 6 mL of pre-equilibrated slurry of Strep-tag Tactin column material (50% Strep-tag Tactin in storage buffer) for 1 h (mixed at 200 rpm on a rotary shaker) at room temperature. The column was washed with 3 x 1 CV (column volume) of resuspension buffer (same as wash buffer used before), and eluted with 6 x 0.5 CV of resuspension buffer containing 2.5 mM desthiobiotin. Fractions were analyzed on a 12% polyacrylamide SDS-Tris Tricine gel followed by Coomassie staining. The concentration of the proteins were determined by using the calculated extinction coefficient $\epsilon_{280} = 25440 \text{ M}^{-1} \text{ cm}^{-1}$ (for all mutants except F93Y and F93W), $\epsilon_{280} = 26930 \text{ M}^{-1} \text{ cm}^{-1}$ for F93Y and $\epsilon_{280} = 30940 \text{ M}^{-1} \text{ cm}^{-1}$ for F93W. Calculations were done by ProtParam on the Expasy server^[4]. Expression yields typically were 10-20 mg/L.

Figure S1 SDS-page gels of the Strep-Tag purification LmrR mutants

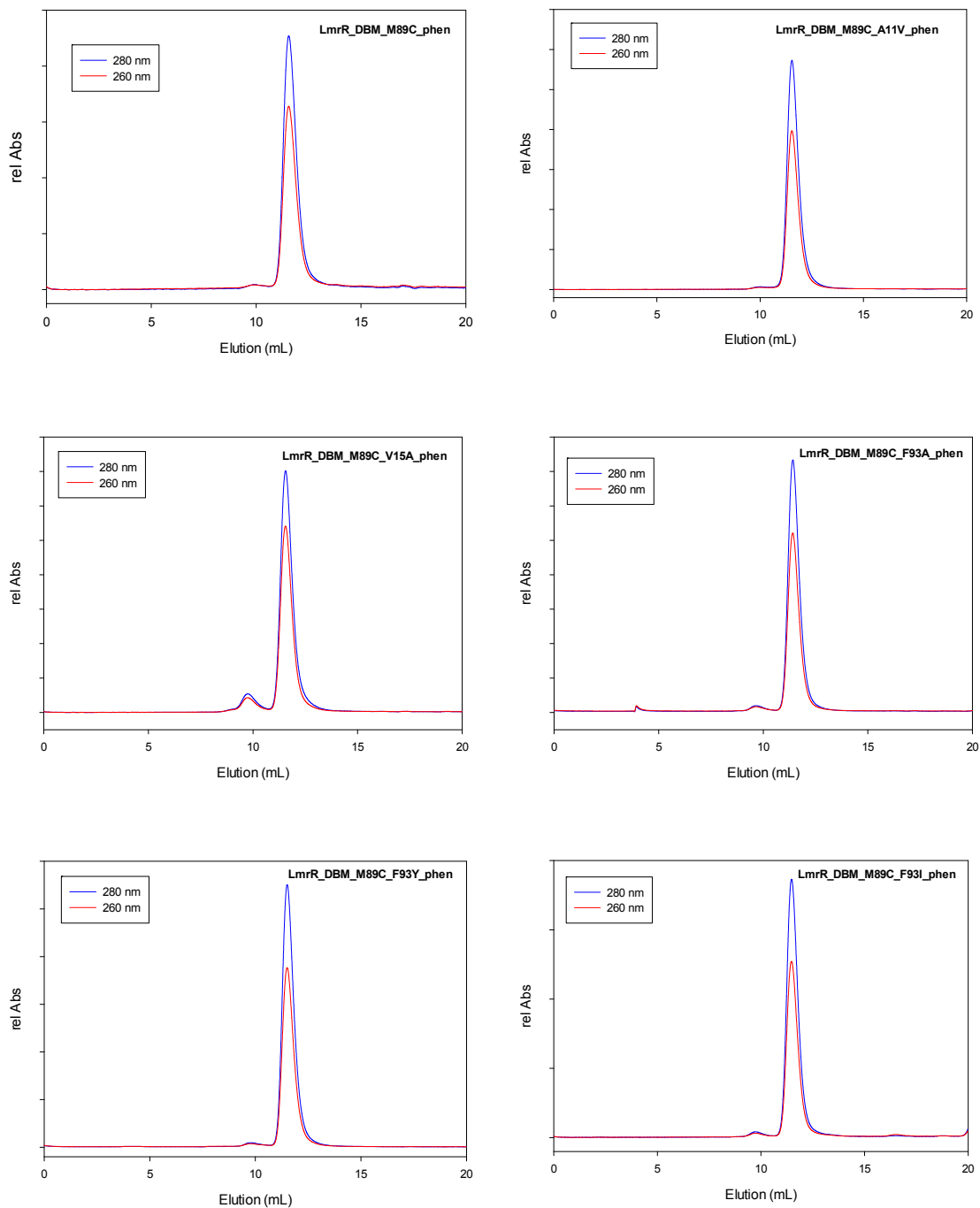




Procedure for the conjugation of the bromoacetamide functionalized phenantroline to the cysteine mutants. The protein was dialyzed against 1L of degassed 50 mM NaH_2PO_4 , pH 7.75, 150 mM NaCl buffer overnight. An 8 times molar excess of **1** dissolved in a small amount of DMSO was added to the protein solution under nitrogen and in the dark. The solution was mixed overnight at 4 °C. The reaction mixtures were rebuffed to 20 mM MOPS, pH 7, 150 mM NaCl buffer using a NAP-10 column. During this procedure excess of **1** was also removed. The efficiency of coupling was determined by an Ellman's test.^[5] A typical Ellman's test: 50 μL of DTNB stock solution (50 mM sodium acetate, 2 mM 5,5'-dithio-bis(2-nitrobenzoic acid) in water), 100 μL 1 M Tris.HCl, pH 8, 40 μL of the sample and 810 μL of H_2O were mixed and absorbance at 412 nm was measured. Using the extinction coefficient ($\epsilon_{412} = 13600 \text{ M}^{-1} \text{ cm}^{-1}$) the amount of free thiols was determined. The concentration of the constructs were determined by the calculated extinction coefficient^[4] and corrected for the absorbance of the ligand. The correction factor was determined by a standard Bradford assay using 'wildtype' LmrR as standard.

Characterization of the LmrR constructs containing Cu-Phen. Analytical size exclusion chromatography was performed on a Superdex 75 10/300 GL (GE Healthcare). $\text{opt_LmrR_X_}[\text{Cu(Phen)(NO}_3)_2]$ was prepared as follows: opt_LmrR_X was added to a $[\text{Cu(Phen)(NO}_3)_2]$ solution (1:1) and incubated on ice for 0.5 hour prior injection (concentrations as in the catalytic reactions). 50 μL of the sample was injected using 20 mM MOPS, pH 7, 150 mM NaCl as buffer (flow 0.5 mL/min). The column was calibrated using the standard Gel Filtration LMW Calibration Kit of GE Healthcare.

Figure S2: Analytical size exclusion chromatography (Superdex-75 10/300 GL) LmrR_X constructs



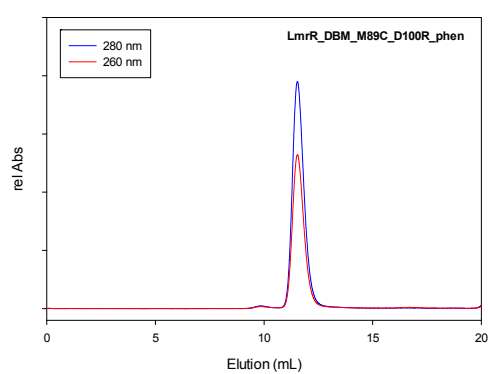
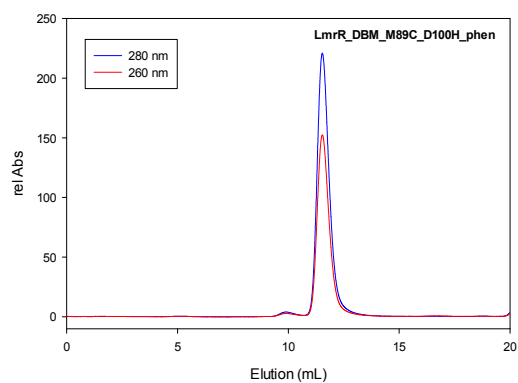
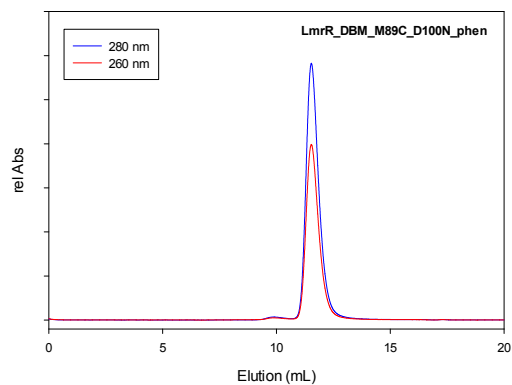
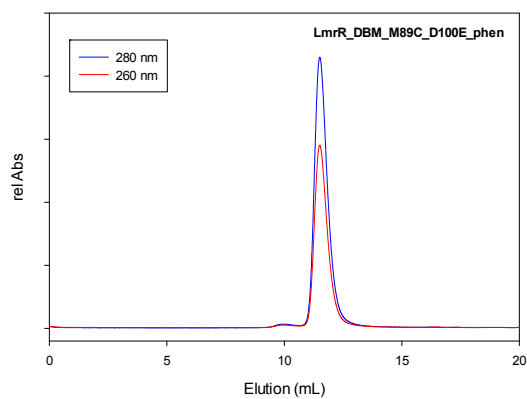
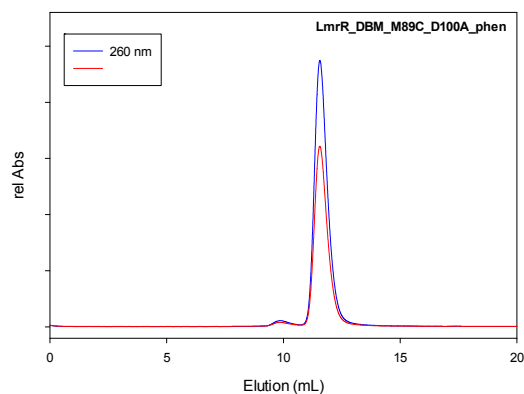
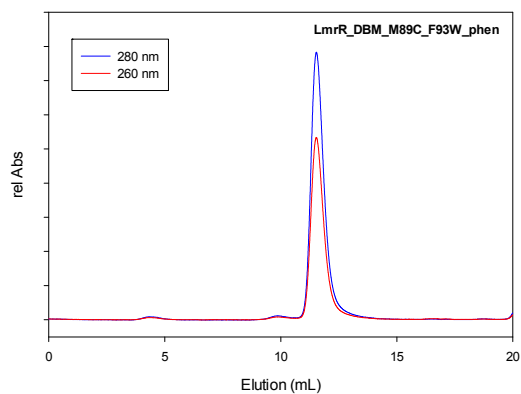


Table S2: Comparison of LmrR_M89C and LmrR_K55D_K59Q in purification.

Construct	<i>Strep-tag Purification</i>	<i>Heparin Purification</i>
	A_{260}/A_{280}^*	A_{260}/A_{280}^*
LmrR_M89C	1.4	0.57
LmrR_K55D_K59Q_M89C	0.58	-

* A_{260}/A_{280} ratio is given as indication of the amount of DNA presence in the purified construct. The LmrR_K55D_K59Q_M89C construct has the same purity in DNA presence after one purification as the LmrR_M89C construct after two purifications.

Figure S2. Asymmetric Diels-Alder reaction catalyzed by LmrR_X.

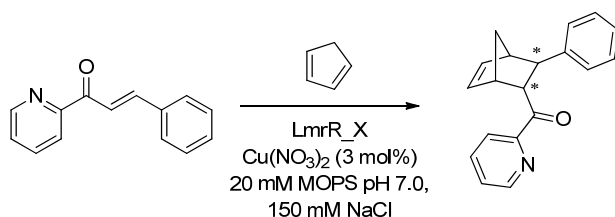


Table S3: Comparison of LmrR_M89C_phen-Cu^{II} and LmrR_K55D_K59Q_M89C_phen-Cu^{II} in the asymmetric Diels-Alder reaction.

Entry	Catalyst*	Conversion [%]	ee (endo) [%]
1	LmrR_M89C_phen-Cu ^{II}	93±4	97±1 (+)
2	LmrR_K55D_K59Q_M89C_phen-Cu ^{II}	89±7	96±1 (+)

* Typical conditions as published previously.

Figure S3. Asymmetric Diels-Alder reaction using 2-acyl imidazoles

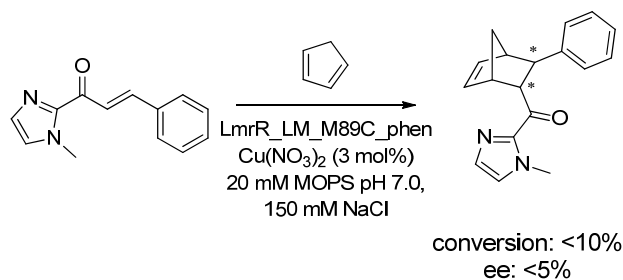
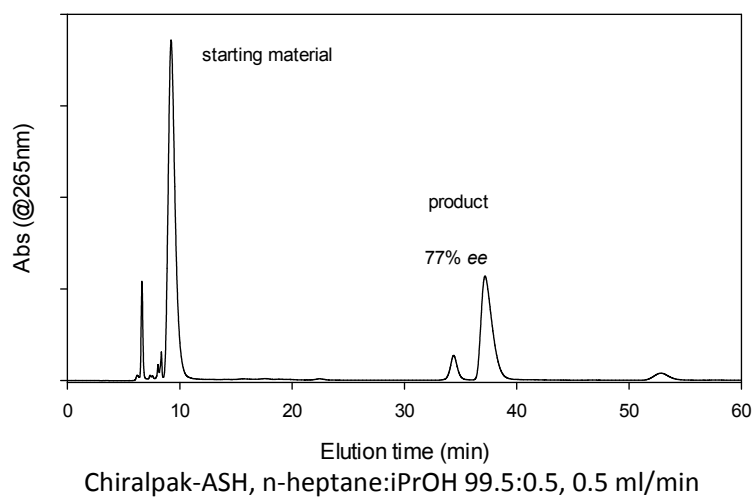
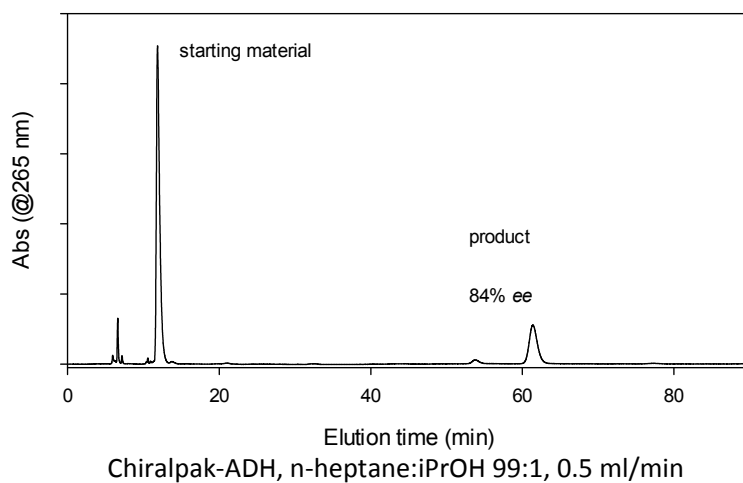


Figure S3: np-HPLC traces of 3a-d catalyzed by LmrR-X constructs

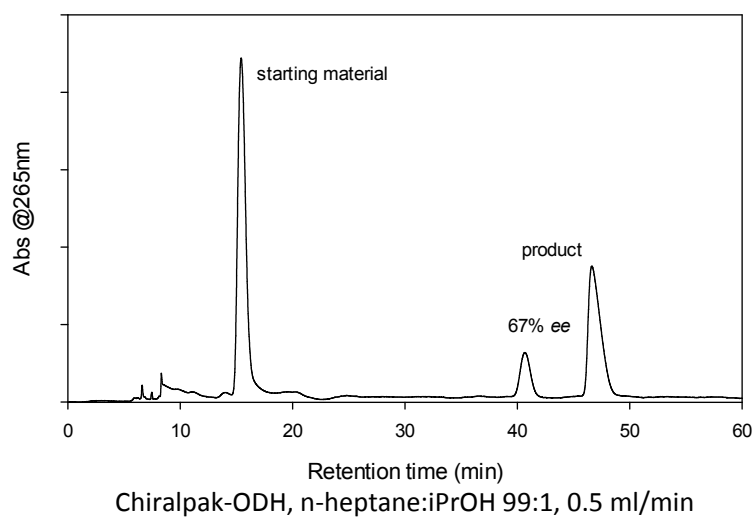
3a



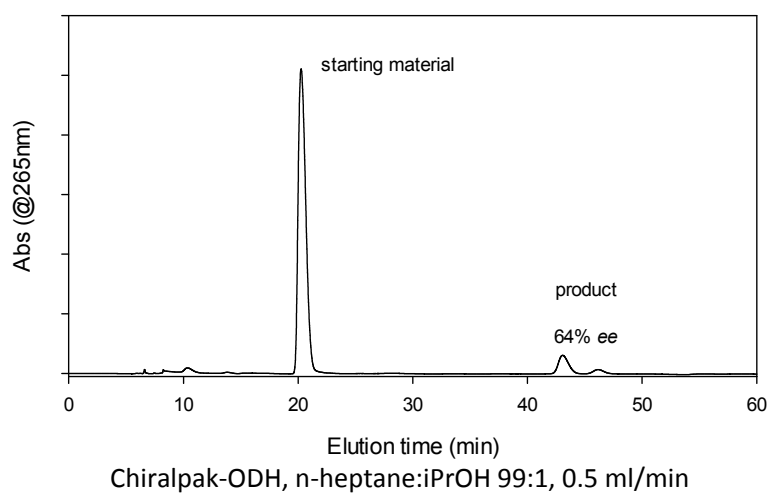
3b



3c



3d



Conversions were calculated using the formula:

$$\text{conv. (\%)} = \frac{\text{area P}}{\frac{\text{area S}}{\text{corr}} + \text{area P}} \cdot 100\%$$

Where *area P* is the total peak area of the product of the reaction, *area S* is the peak area of the starting material and *corr* is the correction factor determined from a calibration curve.

Figure S4. Calibration curves for the determination of the correction factor of 2a, 2b, 2c and 2d.

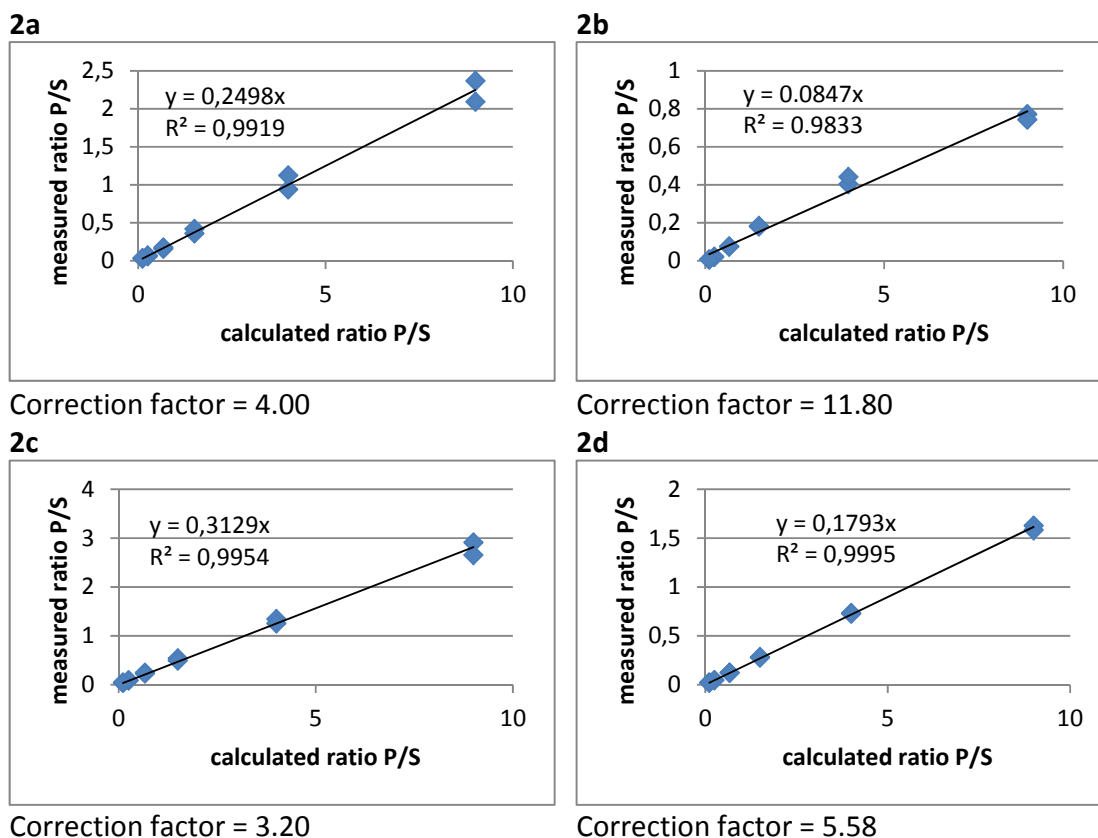
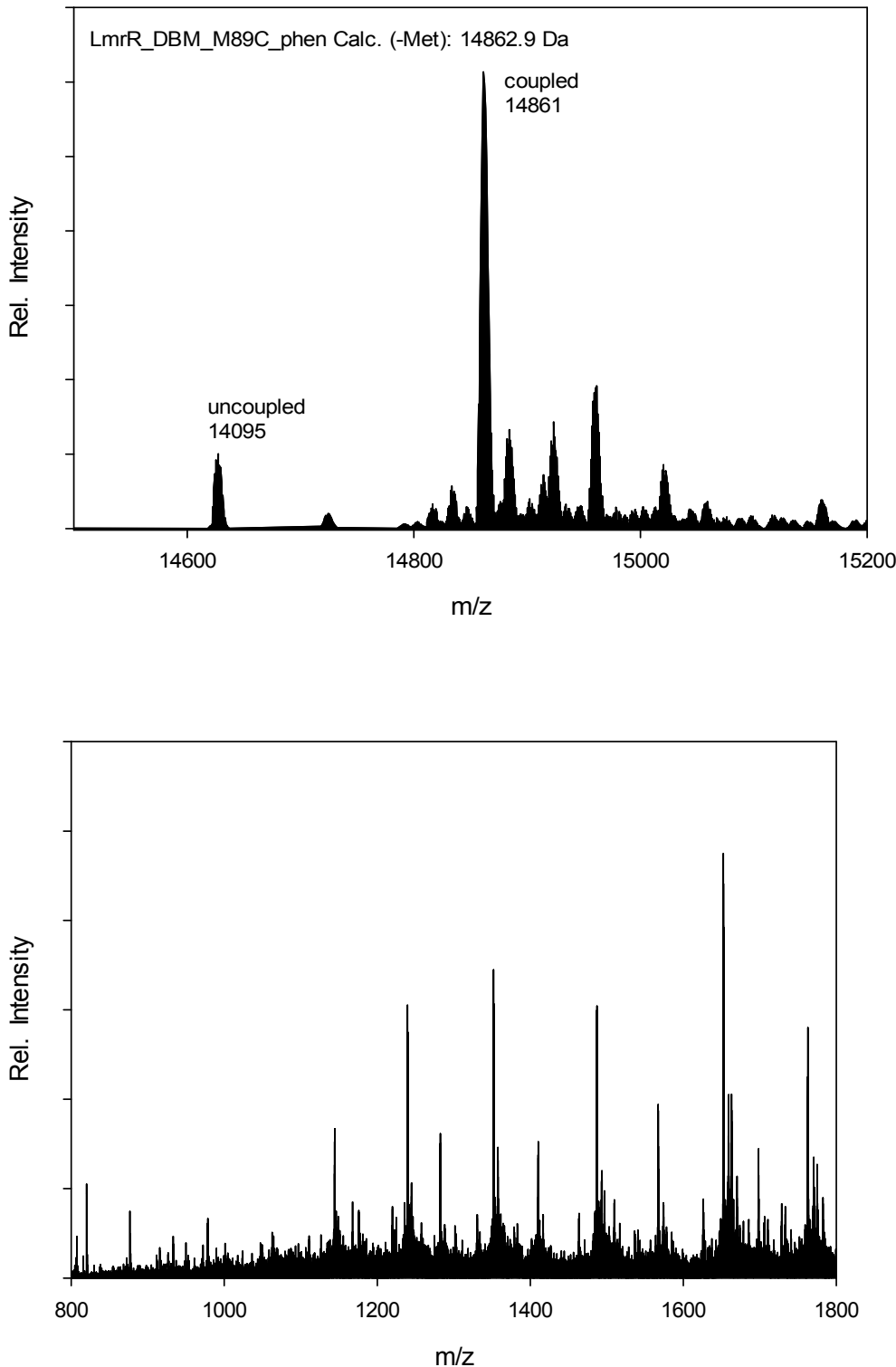
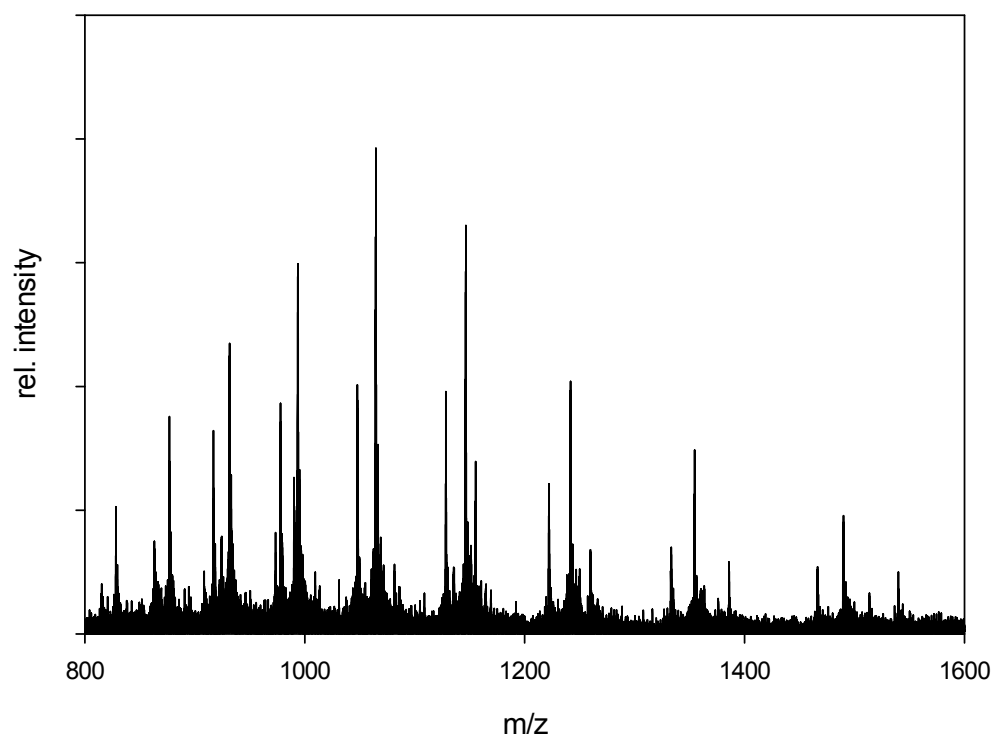
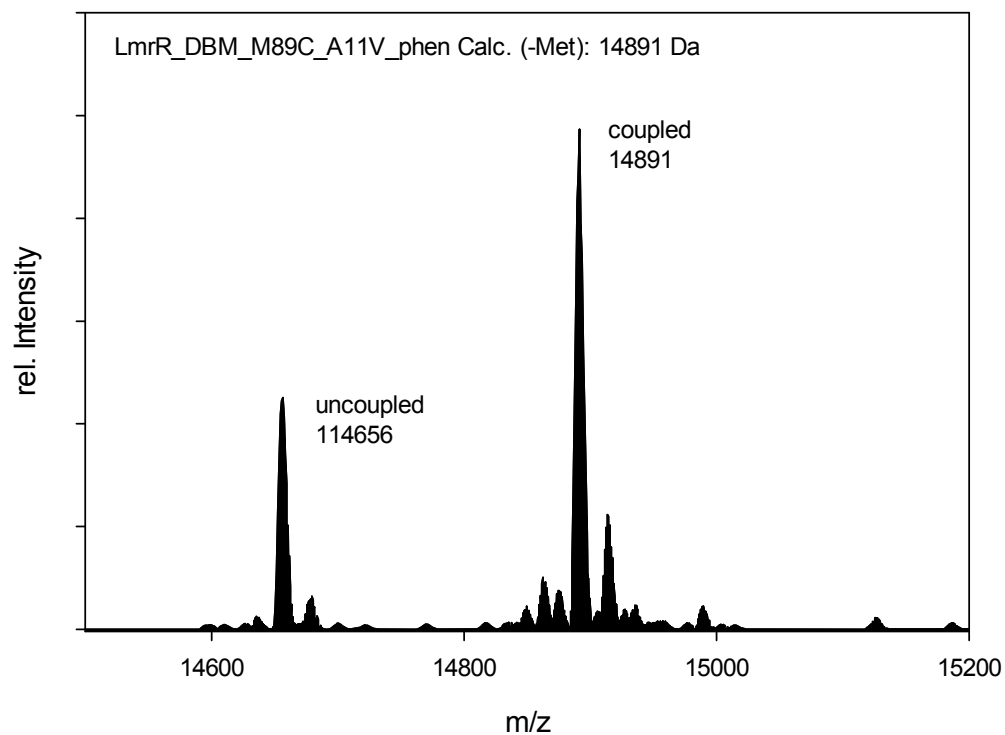
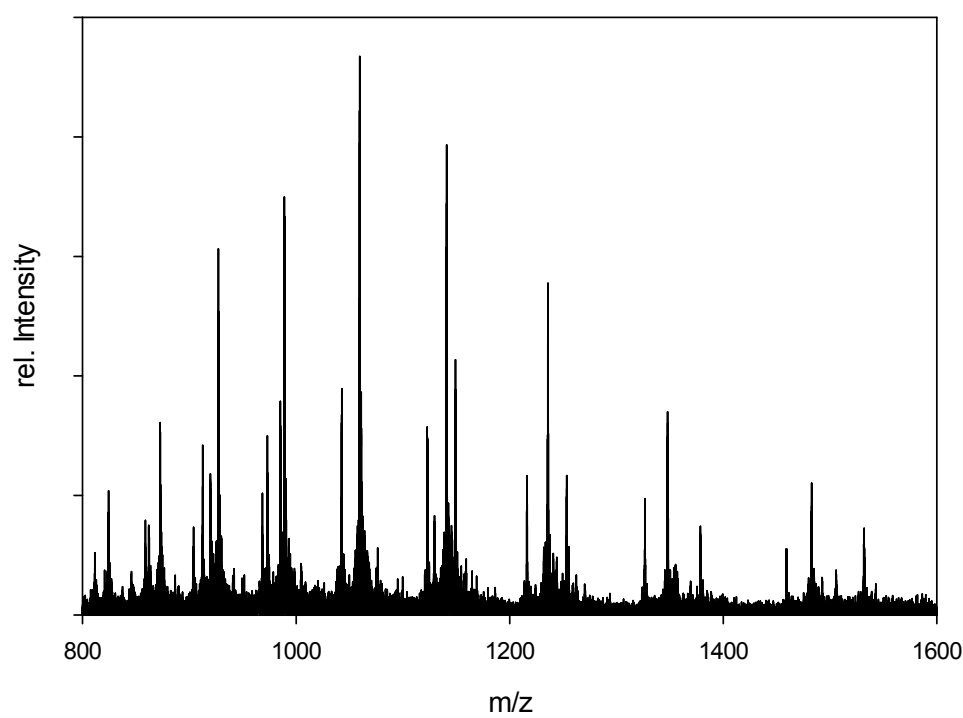
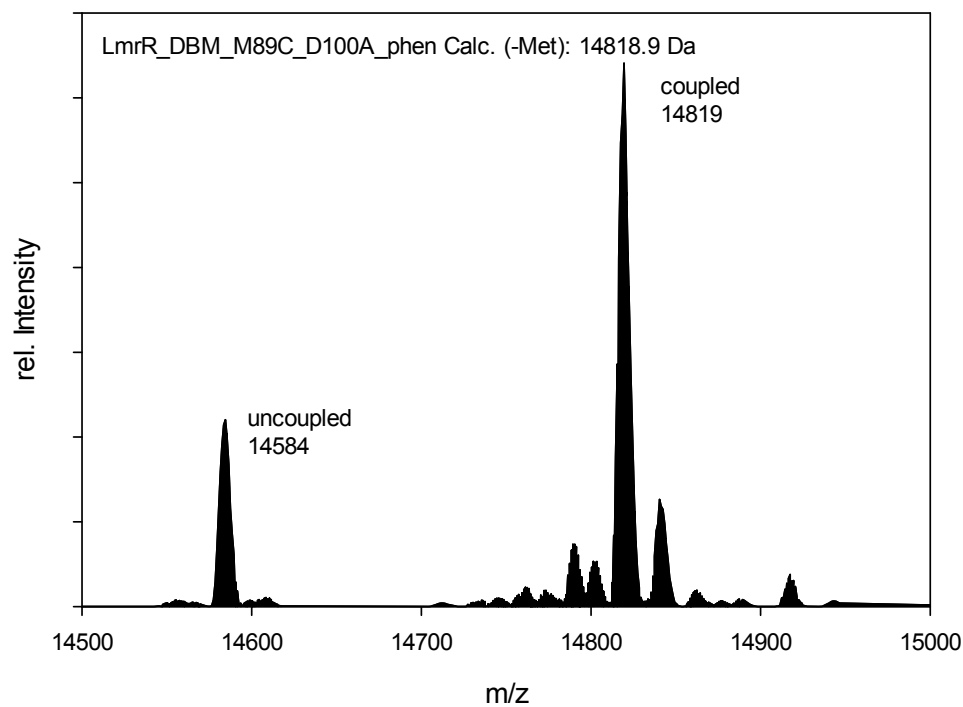
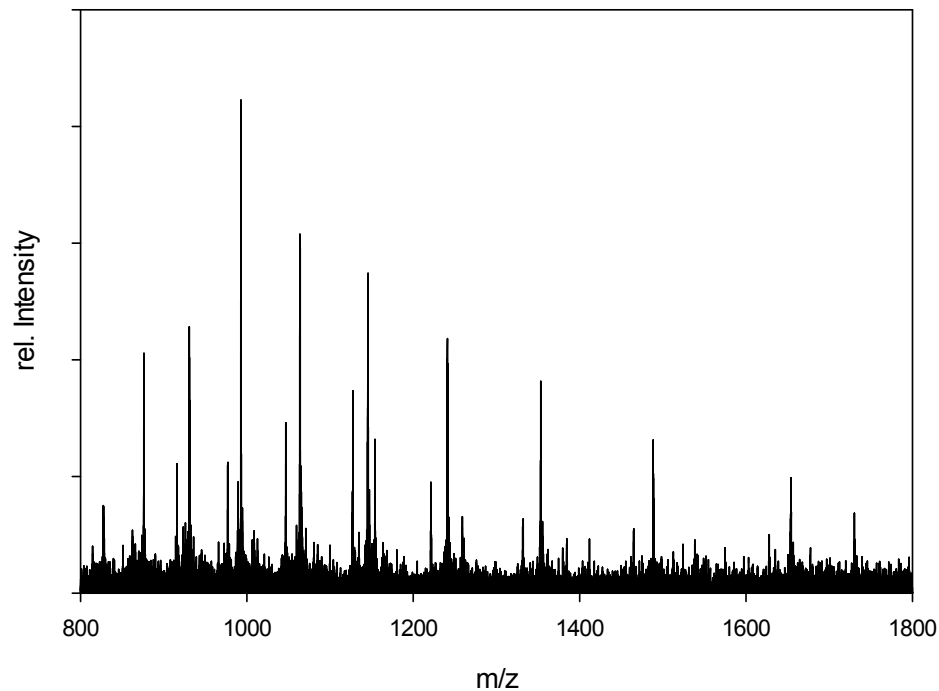
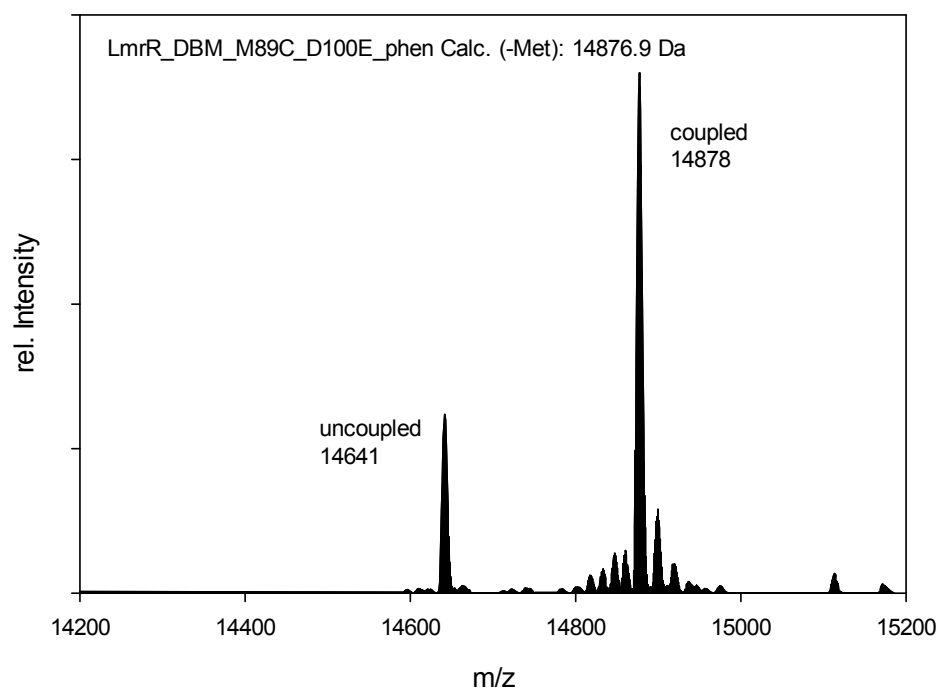


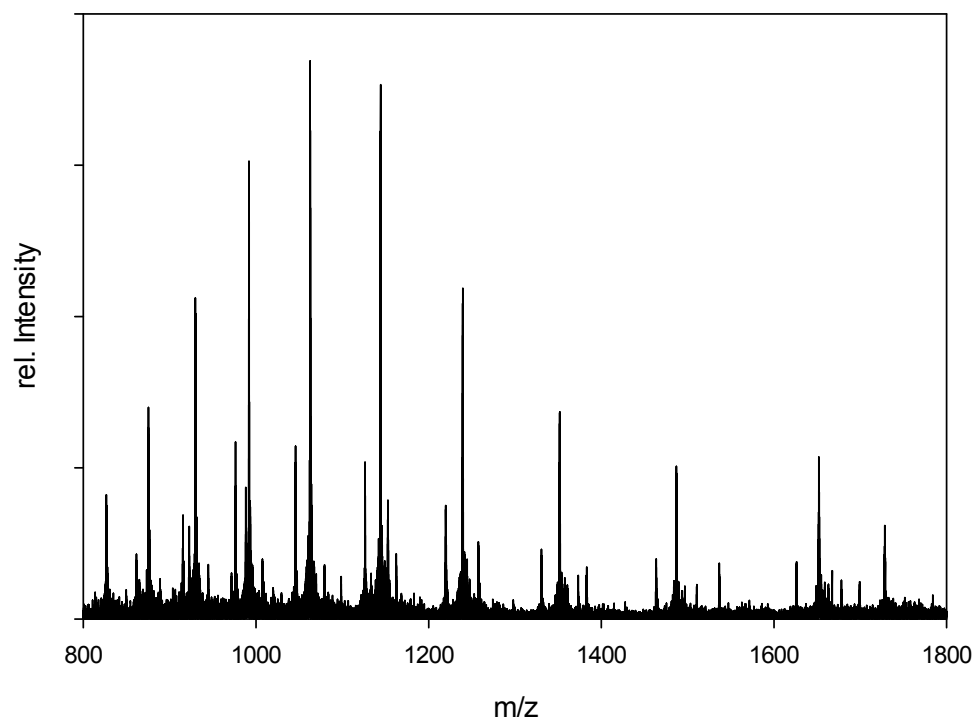
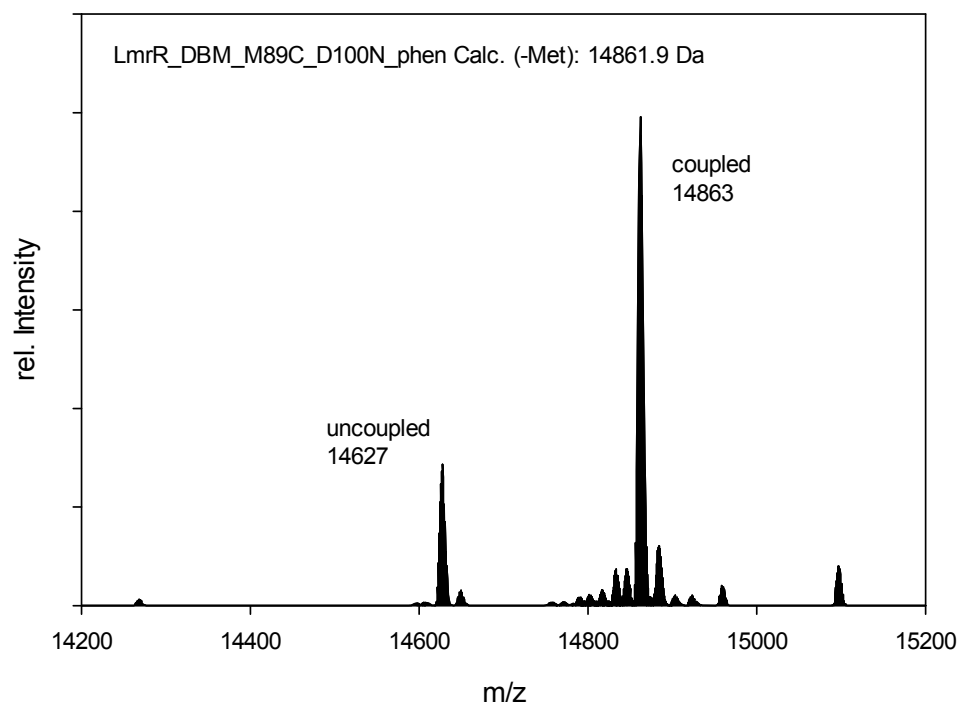
Figure S5. Electrospray ionization (ESI) mass spectra LmrR_X constructs

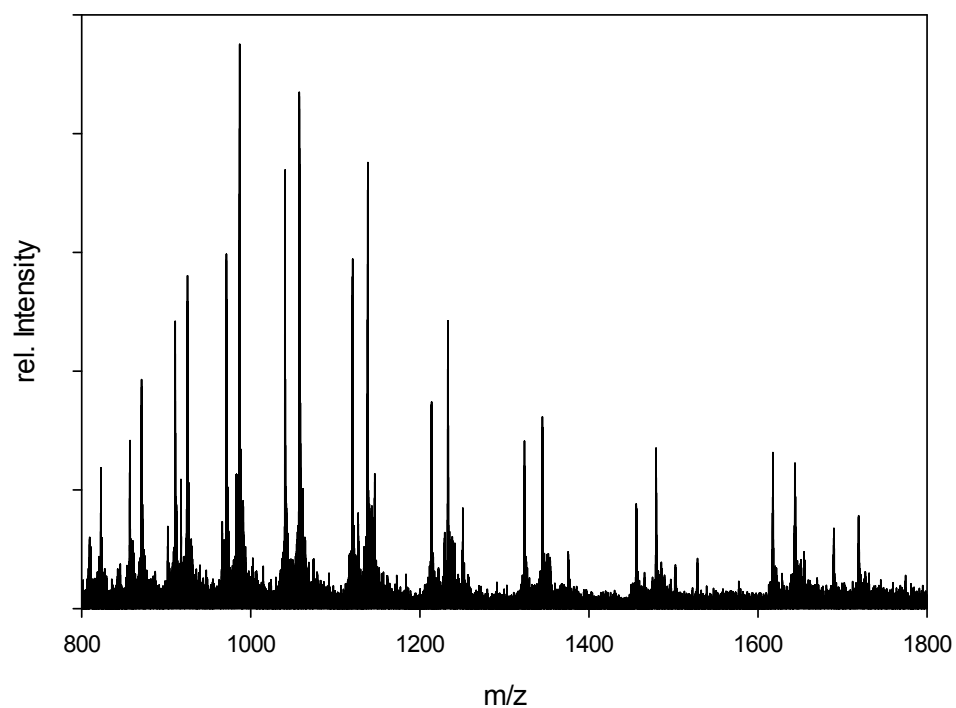
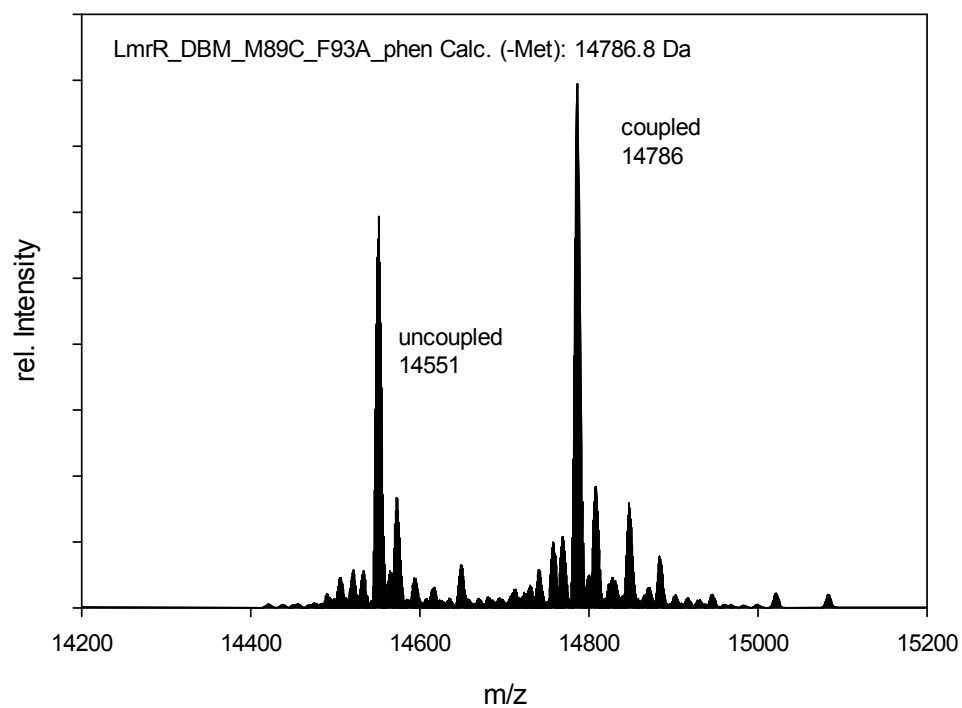


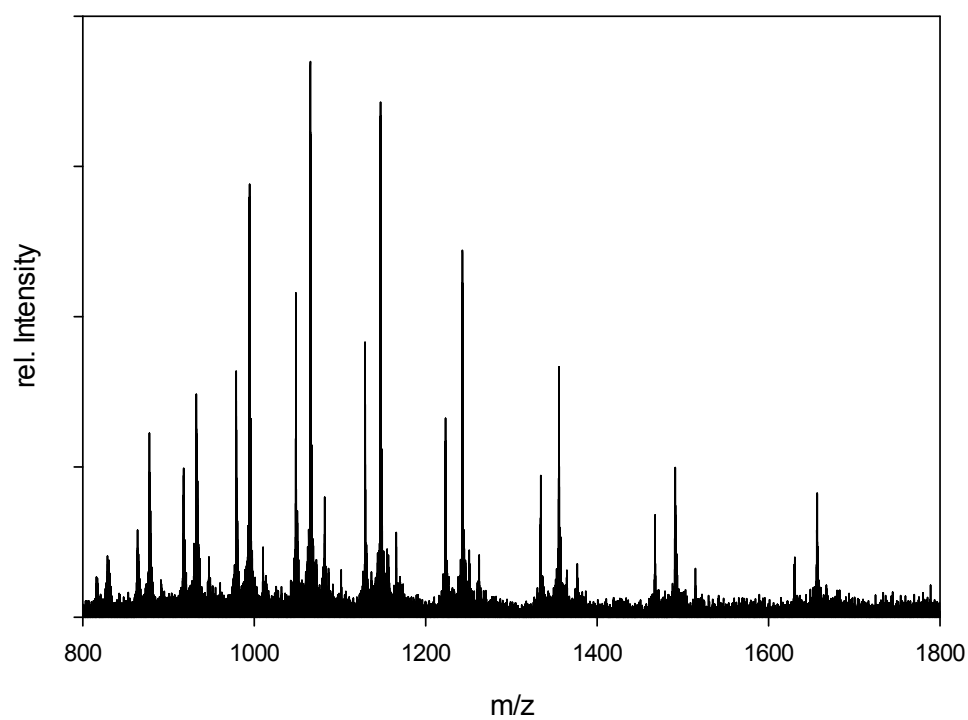
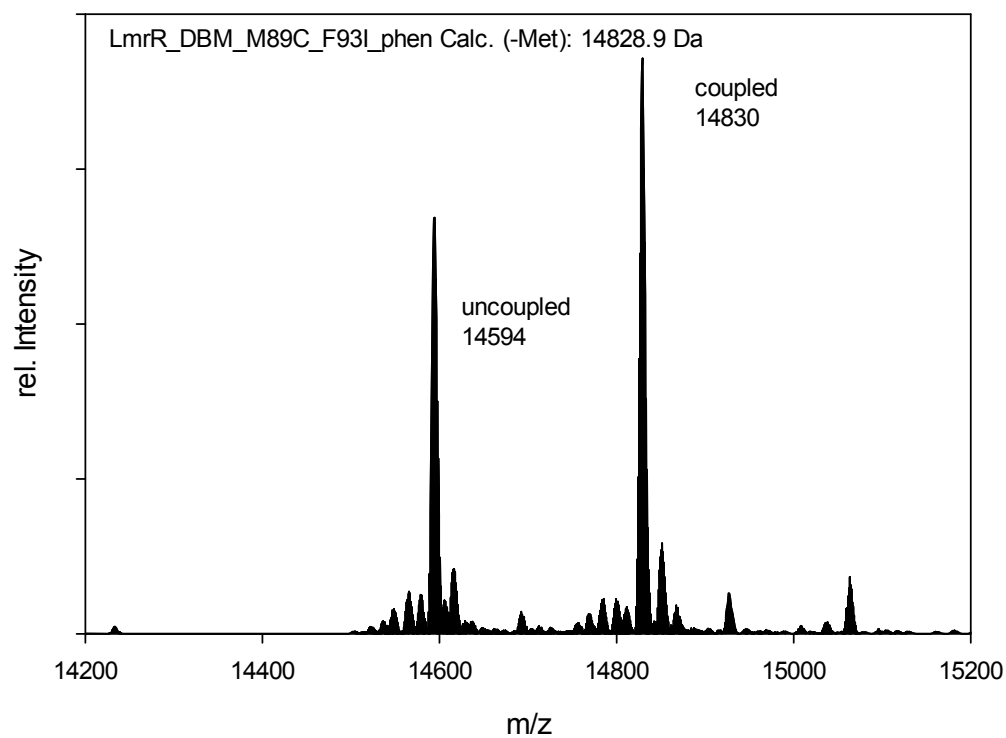


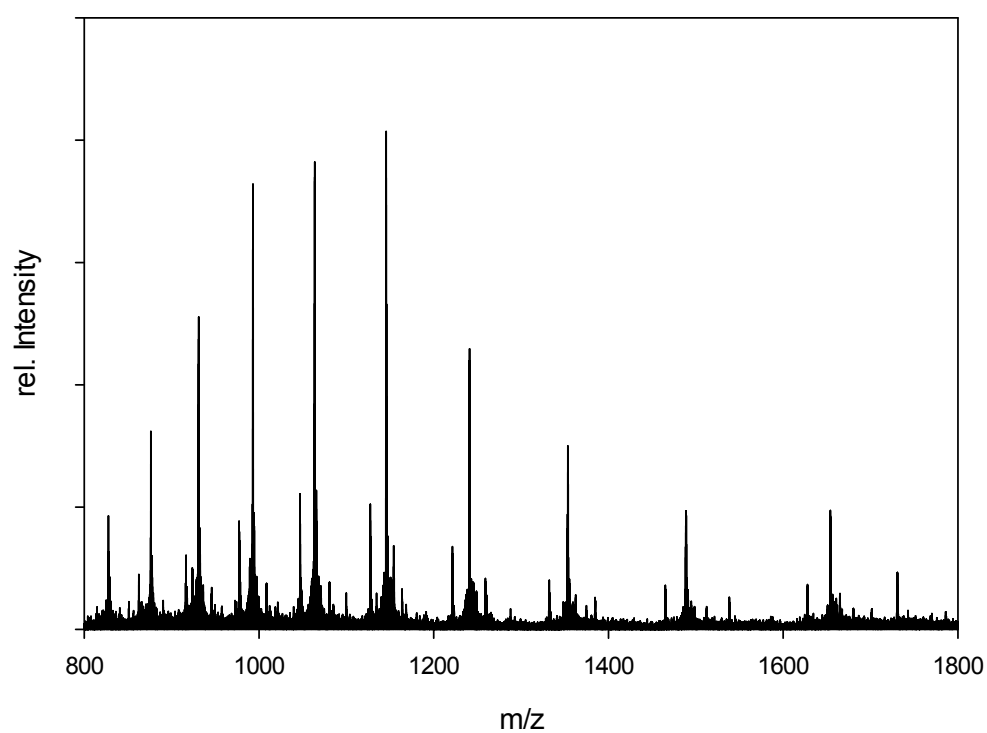
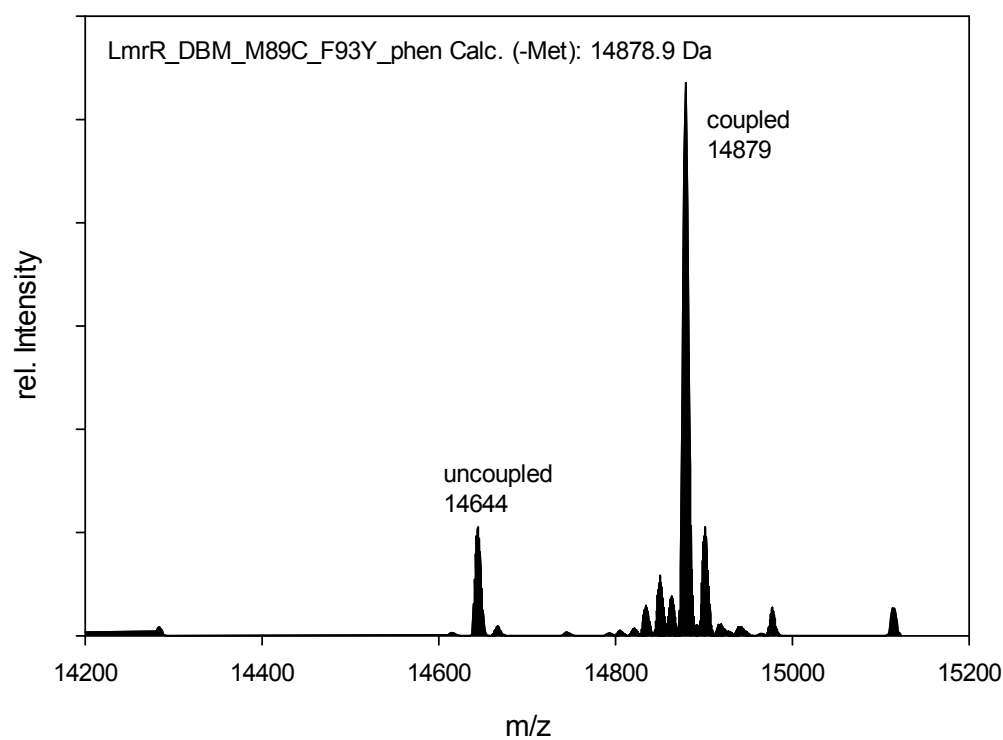


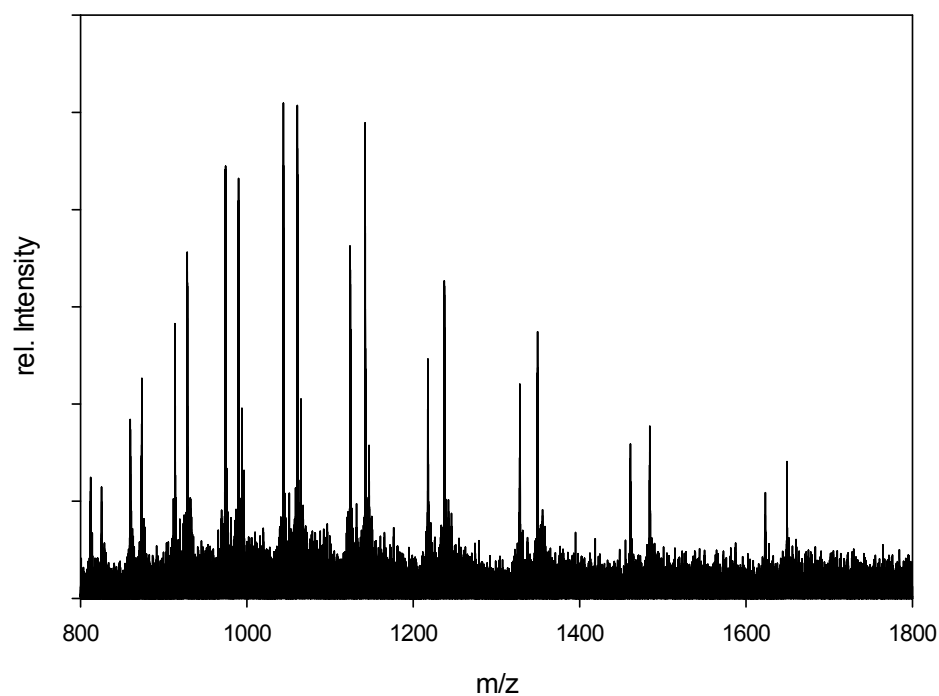
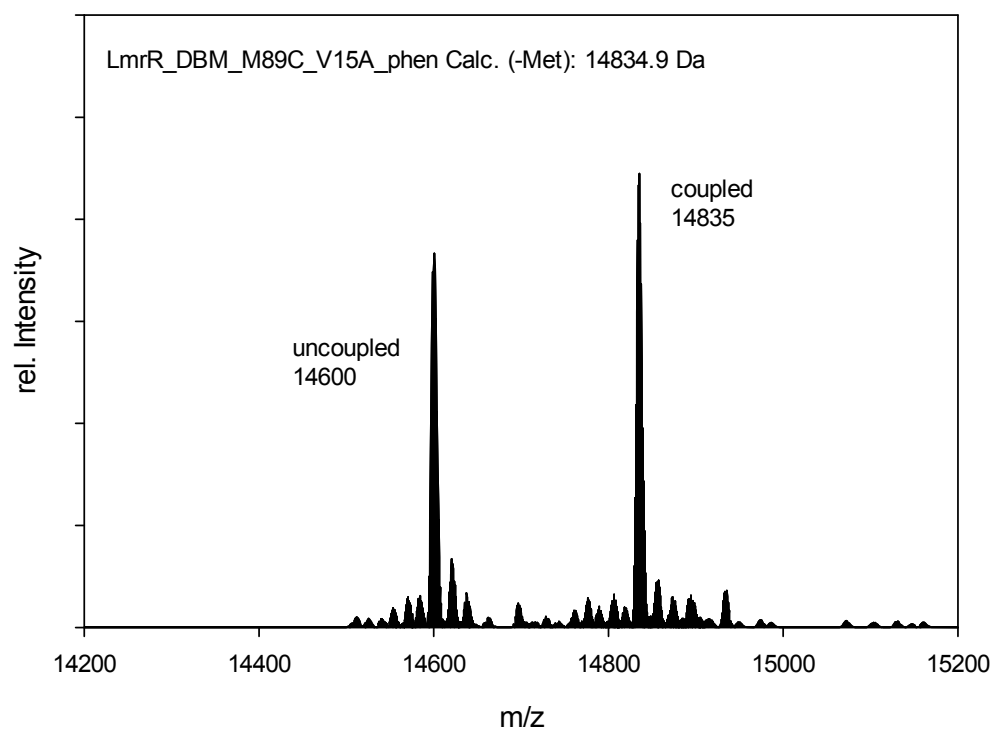












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- [2] C. Fontenas, H. Ait-Haddou, E. Bejan, G. G. A. Balavoine, *Synthetic Communications* **1998**, *28*, 1743-1753.
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